

CHARGE TRANSFER IN CYCLOPOLYMERIZATION AND
THEORETICAL CALCULATIONS FOR CHARGE TRANSFER
IN COPOLYMERIZATION

BY

ROY JOSEPH NOEL VAZ

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1985

ACKNOWLEDGMENTS

I would like to express my deep gratitude to a scholar and gentleman, Dr. G.B. Butler, for his help, stimulation and imparting of wisdom during the course of my stay at the University of Florida. I would like to extend my thanks and appreciation to members of the supervisory committee and to Dr. T.E. Hogen Esch for their time and help.

Appreciation and thanks also go out to Dr. M. Zerner and especially Dr. G. Purvis for their patience, time and help at the Quantum Theory Floor.

All the members of the Polymer Division are greatly acknowledged for their patience and forbearance. Dr. A. Matsumoto is thanked for many helpful discussions.

Friends outside of chemistry are acknowledged for my maintenance of composure.

Thanks are due to Ms. Cindy Zimmerman for the typing of this manuscript.

Financial support from the Department of Chemistry and the National Science Foundation is acknowledged.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENTS.....	ii
LIST OF TABLES.....	v
LIST OF FIGURES.....	vii
ABSTRACT.....	ix
 CHAPTERS	
I INTRODUCTION.....	1
Cyclopolymerization.....	1
Charge Transfer.....	7
Proposed Research.....	12
II EXPERIMENTAL.....	14
General Information.....	14
Reagents and Solvents.....	15
Synthesis of Monomers.....	16
Synthesis of Model Compounds.....	36
Miscellaneous Reactions.....	44
Synthesis of Polymers.....	47
III RESULTS AND DISCUSSION.....	53
NMR Analysis.....	53
Synthesis of Monomers.....	53
Synthesis of Model Compounds.....	77
Comparison of Spectra.....	85
Polymer Synthesis and Characterization.....	100
Conclusions on Polymerization of Monomers.....	104
Frontier Molecular Orbital Analysis.....	108
IV THEORETICAL CALCULATIONS.....	114
Introduction.....	114
Calculation Details.....	118
Discussion.....	135
Conclusions.....	139

APPENDIX	CNDO/2 DENSITY MATRICES AND GROSS CHARGE DENSITIES FOR N-METHYLMALIMIDE, METHYL VINYL ETHER, C ₂ AND C ₃ , RESPECTIVELY.....	141
BIBLIOGRAPHY.....		159
BIOGRAPHICAL SKETCH.....		163

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 Carbon-13 and proton NMR assignments for compound (2).....	60
2 Proton and carbon-13 NMR assignments for compound (4).....	64
3 Proton and carbon-13 NMR assignments for compound (5).....	64
4 Proton and carbon-13 NMR assignments for compound (6).....	65
5 Proton and carbon-13 NMR assignments for compound (7).....	65
6 Carbon-13 and proton NMR assignments for compound (14)....	70
7 Carbon-13 and proton NMR assignments for compound (9).....	70
8 Carbon-13 and proton NMR assignments for compound (11)....	71
9 Carbon-13 and proton NMR assignments for compound (10)....	73
10 Carbon-13 and proton NMR assignments for compound (16)....	79
11 Proton and carbon-13 NMR assignments for compound (20)....	83
12 Proton and carbon-13 NMR assignments for compound (19)....	83
13 Proton and carbon-13 NMR assignments for compound (18)....	84
14 Proton and carbon-13 NMR assignments for compound (21)....	87
15 Comparative proton and carbon chemical shifts for compounds (3) and (16).....	89
16 Comparative proton and carbon chemical shifts for compounds (8) and (17).....	90
17 Comparative proton and carbon chemical shifts for compounds (15) and (21).....	91

18	Comparative carbon chemical shifts for fumaronitrile and 2,4,6-trimethoxystyrene separate and mixed in a 1:1 molar ratio.....	95
19	Comparative proton chemical shifts for fumaronitrile and 2,4,6-trimethoxystyrene separate and mixed in a 1:1 molar ratio.....	96
20	^{13}C chemical shift differences with acceptors different...	97
21	^{13}C chemical shift differences with donors different.....	97
22	Comparison of CNDO and PCILO determinations with experimental data, ΔE -kcal/mole, R-A.....	117
23	Parameters of methyl vinyl ether.....	119
24	Parameters of N-methylmaleimide.....	120
25	Coordinates of C_2 and C_3	122
26	Bond angles and distances (\AA) of C_2	123
27	Bond angles and distances of C_3	125
28	Energy gradient values of last cycle and summary of geometry optimization of cycles 95-106 for methyl vinyl ether.....	127
29	Energy gradient values of last cycle and summary of geometry optimization of cycles 38-46 for N-methylmaleimide.....	128
30	Energy gradient values of last cycle and summary of geometry optimization of cycles 155-156 for C_2	129
31	Energy gradient values of last cycle and summary of geometry optimization of cycles 167-170 for C_3	130
32	CNDO energy and difference in energy corresponding to various distances between molecules N-methylmaleimide and methyl vinyl ether.....	133
33	PCILO energy and difference in energy corresponding to various distances between molecules N-methylmaleimide and methyl vinyl ether.....	137
34	Coordinates of the complex ($\text{E}_{\text{C}*}$) with the moieties at a distances of 7.0 \AA	138

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1	Reaction coordinates proposed as a result of product distribution study in the cyclization of radicals XII and XIII.....8
2	Evidence for charge transfer between acrylonitrile and styrene in the presence of $ZnCl_2$11
3	Apparatus for the pyrolysis of chloroacetone cyanohydrin acetate.....23
4	Proton spectrum of the pyrolysis products with the integration (in $CDCl_3$).....24
5	HPLC chromatograph. Separation of 2-phenylallyl 2'-cyanoallyl ether.....27
6	Proton (60 MHz) spectrum in $CDCl_3$32
7	HPLC chromatograph. Separation of 2-phenyl 2'-carboethoxyallyl ether.....37
8	Information regarding C 13 NMR chemical shifts of substituted alkenes.....54
9	Proton (100 MHz) spectrum and noise decoupled C 13 spectrum of compound (1) in $CDCl_3$58
10	Proton (100 MHz) spectrum (in $CDCl_3$) and C 13 noise decoupled 25 MHz spectrum (in benzene- d_6) of compound (3).....61
11	Proton spectrum (100 MHz)(in benzene- d_6) and C 13 noise decoupled spectrum (25 MHz)(in $CDCl_3$) of compound (8).....66
12	25 MHz decoupled and multiplicity determination C 13 spectra for compound (8).....67
13	Carbon-13 (25 MHz) spectrum of the pyrolysis of 1-bromo-2,2-dimethoxy propane.....74

14	Proton spectrum (60 MHz) in CDCl_3 (15).....	75
15	Noise and off-resonance decoupled C 13 spectra in CDCl_3 (15).....	76
16	Proton (100 MHz) NMR spectrum (in CDCl_3) and carbon-13 (25 MHz) NMR spectrum (in CDCl_3) of compound (17).....	81
17	25 MHz decoupled and multiplicity determination sequence C 13 spectra (21).....	86
18	Analysis for explanation of observed shifts.....	92
19	Synthesis scheme used for 2,4,6-trimethoxystyrene.....	93
20	UV of compound (15)(conc = 10^{-5} M) in t-butyl alcohol at different temperatures.....	99
21	GPC curves for polymers (in DMF) formed at different temperatures.....	101
22	Proton NMR for polymers (in CDCl_3) formed at 40° C and 60° C.....	102
23	Carbon-13 NMR spectra for polymers formed at 40° C and 60° C.....	103
24	GPC curves for polymers (in DMF) formed at R.T. and 40° C.....	105
25	Frontier orbital energies and coefficients of ethylene and monosubstituted ethylenes.....	109
26	Representation of the systems studied.....	111
27	Z-axis view of ZINDO geometry optimized molecules.....	121
28	Z-axis view of ZINDO geometry optimized molecules.....	131
29	Plot of $\Delta E_{\text{comp1}} = E_{\text{C}} - (E_1 + E_2)$ vs. distance.....	134
30	Plot of $\Delta E_{\text{comp1}*} = E_{\text{C}*}(r) - E_{\text{C}*}(\infty)$ vs. distance.....	136

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

CHARGE TRANSFER IN CYCLOPOLYMERIZATION AND
THEORETICAL CALCULATIONS FOR CHARGE TRANSFER
IN COPOLYMERIZATION

BY

ROY JOSEPH NOEL VAZ

August, 1985

Chairman: Dr. George B. Butler
Major Department: Chemistry

Continuing studies on the mechanism of cyclopolymerization lead to the inclusion of charge transfer complexes in the monomer in order to influence the ring size. It was anticipated that if a donor and acceptor group were substituted at the C_2 and $C_{2'}$ positions, respectively, of an allyl ether, an intramolecular complex would be formed.

Monomers selected for the study were 2-chloroallyl 2'-phenylallyl ether, 2-carboethoxyallyl 2'-phenylallyl ether, 2-cyanoallyl 2'-phenylallyl ether and 2-carboethoxyallyl 2'-methoxyallyl ether. Intramolecular charge transfer complexation was proved by omitting the point of unsaturation having the donor group. For this study 2-carboethoxyallyl 2'-phenylpropyl ether, 2-cyanoallyl 2'-phenylpropyl ether and 2-carboethoxyallyl 2'-methoxypropyl ether were synthesized

and the carbon-13 and proton NMR spectra were compared with those of the corresponding monomers in order to determine "charge transfer."

The monomers were polymerized with 2,2'-azobisisobutyronitrile in benzene and only 2-carboethoxyallyl 2'-phenylallyl ether gave a linear cyclopolymer soluble in most organic solvents. 2-Chloroallyl 2'-phenylallyl ether did not afford any polymer and 2-cyanoallyl 2'-phenylallyl ether and 2-carboethoxyallyl 2'-methoxyallyl ether afforded branched polymer when the percentage conversion and percent monomer concentration were kept low. This was determined via gel permeation chromatography.

The polymer of 2-carboethoxyallyl 2'-phenylallyl ether consisted largely of five-membered rings at 40° C and six-membered rings at 60° C. This ring distribution supports intramolecular "charge transfer" complexation at lower temperatures and the normal cyclopolymerization dominating at higher temperatures corresponding to the charge transfer complex breaking up.

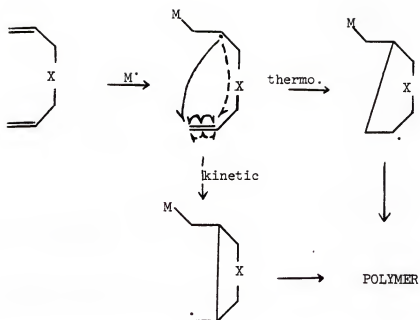
Theoretical calculations such as geometry optimizations were carried out on N-methylmaleimide and methyl vinyl ether and possible complexes involving them in order to support charge transfer between these two molecules.

CHAPTER I INTRODUCTION

Cyclopolymerization

History

Early in the history of Polymer Science, a general principle was established by Standinger¹ that polymerization of nonconjugated dienes leads to crosslinked and therefore non-soluble, nonlinear polymers or copolymers. An exception to this widely accepted principle was observed by Butler,² who found that a variety of diallyl quarternary ammonium salts polymerized to yield soluble, and hence linear polymers containing little or no residual unsaturation. To account for these, Butler and Angelo³ suggested a polymerization mechanism that involves an alternating intermolecular-intramolecular chain propagation. The six-membered structure proposed for radical initiated cyclopolymerization of 1,6 dienes was based upon the generally accepted hypothesis advanced by Flory⁴ regarding the predominance of the more stable radical in controlling the course of vinyl polymerization. Intervening studies have shown that in numerous cases cyclopolymerizations do not adhere to this hypothesis but lead to cyclic structures derived via propagation through the less stable intermediate, i.e., reactions proceeded via kinetic rather than thermodynamic control (Scheme 1).



Scheme 1: Butler scheme for cyclopolymerization.

It has been shown that suitable monomers undergo cyclopolymerization via all of the well known methods of initiation of polymerization.²

A type of copolymerization constitutes a significant portion of the cyclopolymerization literature.² This process, referred to as cyclocopolymerization, incorporates both comonomers into the developing cyclic structure. The most extensively studied example of this unusual type of copolymerization is the cyclocopolymer of divinylether and maleic anhydride. This copolymer has been extensively studied for its biological properties.⁵

Monomers having two different functional groups have been studied in cyclopolymerization.²

Cyclopolymerization of diene monomers leading to larger (>7) rings has also been studied.²

Mechanism of Radical Cyclopolymerization

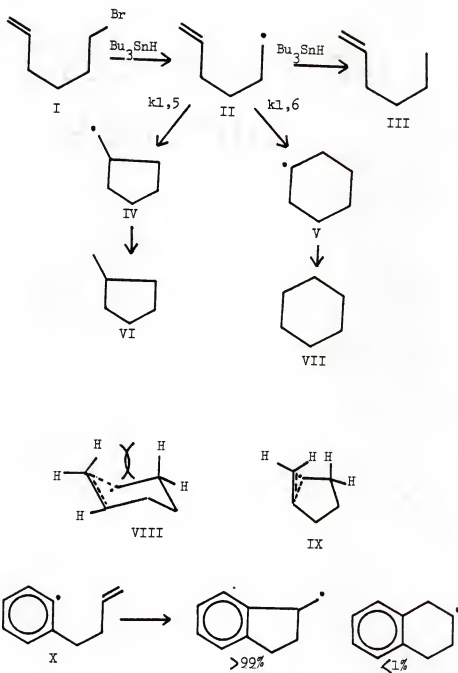
Important aspects of the process are embodied in a kinetic study carried out on methacrylic anhydride.⁶ This study showed that the intramolecular cyclization step is higher in energy by 2.6 kcal/mole than the intermolecular step. The rate of cyclization, however, was found to be considerably faster than the intermolecular propagation step in support of a very high steric factor favoring cyclization. Bimolecular reactions involve substantial loss of translational entropy whereas intramolecular reactions only involve the loss of internal rotational degrees of freedom and are therefore favored. The thermochemical approach to the explanation of ring sizes failed.

Less favored ring sizes may be formed in cyclopolymerization and the less stable radical may predominate in the cyclization. The model hex-5-enyl radical (I) (Scheme 2) has been studied extensively and various propositions⁷ with regard to the formation of the less stable radical (IV) being formed faster have come under consideration. Notably they could be listed as:

- (1) entropy of activation^{8,9,10}
- (2) unfavorable non-bonded interaction¹¹
- (3) stereo electronic factors

(1) The entropy change associated with the loss of rotational freedom in intramolecular reactions becomes unfavorable with increasing size of the ring being formed. The magnitude of this difference ($\sim 3.4 \text{ cal mol}^{-1}\text{K}$) at ordinary temperatures is far too small to account for the degree of regioselectivity exhibited by the ring closure reaction and hence is not a dominant factor though it could not be ruled out. The favorable enthalpy of activation ($\sim 1.7 \text{ kcal/mole}$) is also not a dominant factor.

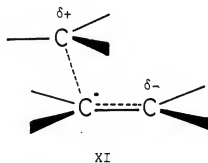
(2) The Julia-LeBel hypothesis. An unfavorable non-bonded interaction between the pseudo-axial proton at C_2 and the syn proton at C_6 will destabilize the transition state (VIII) for 1,6 ring closure by comparison with (IX) for five-membered ring formation. The magnitude of the interaction ($< 0.8 \text{ kcal mol}^{-1}$) is not sufficient to account for the high preference for 1,5 ring closure besides alkenyl radicals (X) having no pseudo-axial proton at C_2 undergo regiospecific formation of a five-membered ring.¹²



Scheme 2: Reactions of the hex-5-enyl radical (I).

(3) The stereo electronic theory contends that the strain engendered in accommodating the mandatory disposition of reactive centers within the transition complex for 1,5 ring closure outweighs those steric and thermochemical factors expected to favor the formation of the more stable possible product. It involves the structure (XI) where the dominant interaction for attack of an alkyl radical on an olefinic bond involves overlap of the semi-occupied 2p orbital with one lobe of the vacant π^* orbital.^{13,14}

A structural feature which affects the ability of an unsaturated radical to accommodate the intimate transition complex for addition will necessarily affect also the rate and regreoselectivity of ring closure, e.g., shorter bonds (C-O, C-N) favors 1,5 ring closure.



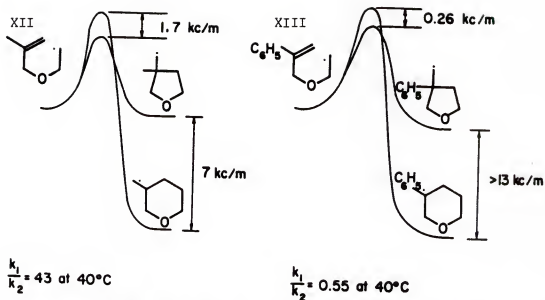
Substituents at C_5 (XII) do not enhance 1,6 ring closure but rather retard 1,5 ring closure,¹⁵ suggesting that the formation of the transition complex involves considerable configurational change at C_5 , and that it is this change toward sp^3 hybridization which is effected by substituents (through B strain). However, when the substituent at C_5 is capable of interacting strongly with an adjacent radical center, it may increase the rate of 1,6 ring closure;

nevertheless, it will still retard the rate of 1,5 ring closure. Thus the phenyl substituted radical (XIII) undergoes 1,6 ring closure more rapidly than the parent, but 1,5 ring closure occurs more slowly¹⁶ (Fig. 1).

Substituents at C_1 expected to exert a strong conjugative effect on the adjacent radical center often afford mainly products of 1,6 ring closure. Such results¹⁷ are not incompatible with the concept of stereo electronic control since 1,5 ring closure is the kinetically controlled process, but being truly reversible,¹⁰ it is often superceded by slow but essentially irreversible 1,6 ring closure. Also the transition complexes for these weakly exothermic reactions may lie towards the product end of the ring closure reaction coordinate making stereo-electronic effects less important unlike normally, when ring closure proceeds through a very early transition state in which there is little change of configuration at C_1 or C_6 and little transfer of spin density.¹¹

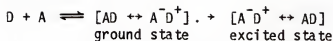
Charge-Transfer

It was Mulliken¹⁸ who first proposed a theory to account for bonding in complexes (donor-acceptor) which do not conform to the Lewis acid-Lewis base description. Mulliken¹⁹ proposed that charge-transfer complexes arise from interaction between donor molecules and acceptor molecules having high-energy filled orbitals (i.e., low ionization potentials, I_D) and acceptors having low energy unfilled orbitals (i.e., high electron affinities, E_A) viz:

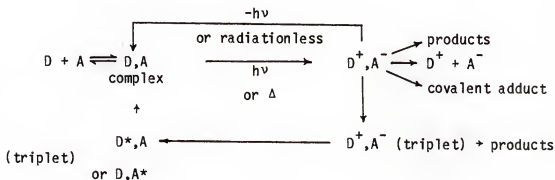


k_1 = rate constant for five-membered ring formation; k_2 = rate constant for six-membered ring formation.

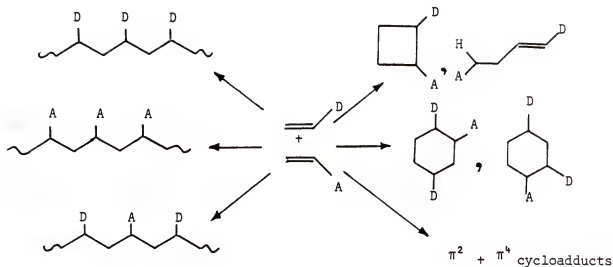
Fig. 1: Reaction coordinates proposed as a result of product distribution study in the cyclization of radicals XII and XIII.



Dewar and Thompson²⁰ suggested that other aspects of these intermolecular combinations, notably the enthalpies of formation, are very similar to those expected on the basis of Van der Waals forces including dipole-dipole, dipole-induced-dipole and dispersion forces. Also, the only requirement that a charge-transfer transition occur is that the species involved be close together. A transition could occur equally well if the components were held together by simple Van der Waals forces, and there is ample evidence for so-called charge-transfer spectra. Kosower²¹ reviewed the possibilities for involvement of charge transfer complexes in organic reactions as exemplified by the following scheme:



The spontaneous thermal reactions of electron rich olefins with electron poor olefins gives a wide diversity of organic and polymer molecules as shown in the scheme below.²²



D = donor: OR, NR_2 , Aryl, etc.

A = acceptor: CN, COOCH_3 , etc.

These spontaneous reactions have been attributed to initiation by charge-transfer complexes or by ion-radicals arising by electron transfer from donor olefin to acceptor olefin.²³ This has been shown not to be true.²⁴ They may be on the reaction path but not in the initiation step.

Butler and Olson²⁵ studied the role of the charge-transfer complex in the propagation step of the copolymerization N-(alkyl) maleimide with vinyl ethers.

Seymour et al.²⁶ have shown the existence of a charge transfer complex between acrylonitrile complexed to a Lewis acid (ZnCl_2) and styrene. The Lewis acid enhances charge transfer. The details are shown in Figure 2.

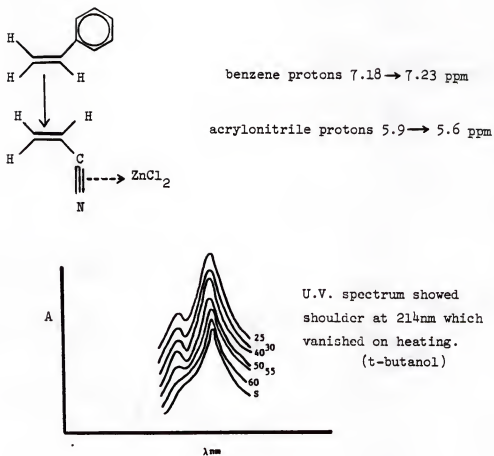


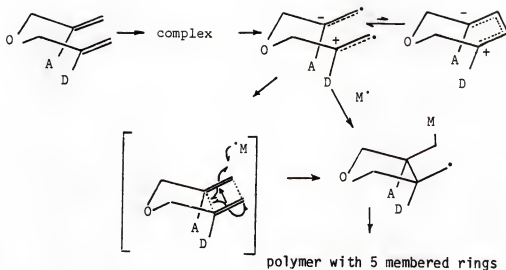
Fig. 2: Evidence for charge transfer between acrylonitrile and styrene in the presence of ZnCl₂.

The stereochemistry of the complex in the presence of strong or multiple donors and acceptor substituents has been visualized^{23,24} such that it could lead to a tetramethylene zwitterion with one end of zwitterion carbon having the donor and the positive charge and the other end having the acceptor and the negative charge. This would lead to the isolation of 1-donor-2-acceptor cyclobutane molecules. This zwitterion is proposed²⁴ to be the live intermediate which leads to small molecules and initiates polymerization.

Frontier molecular orbital theory²⁷ has been invoked to explain the reactivity and consequent stereochemistry of the products in copolymerization of alkenes substituted with an electron donor and an electron acceptor. It has also been used to explain the ring-size in cyclopolymerization since thermodynamic stability is determined by the energies of all the filled orbitals, but kinetic stability is mostly determined by the highest occupied molecular orbital.

Proposed Research

A combination of sections A and B would lead one to propose cyclopolymerization of molecules having intramolecular charge transfer between alkene groups substituted with a donor and an acceptor group and polymerization of the intramolecular complex leading to the intramolecular zwitterion as shown in the following scheme:



If the donor was phenyl, and there was no charge transfer interaction one would expect six-membered ring formation to predominate since the rate of five-membered ring formation was relatively inhibited and the six-membered ring formation favored as explained earlier.¹⁶ The initiation due to the "tetramethylene zwitterion" would complicate matters.²⁴ However, the single donor and acceptor groups used here would be relatively weak such that the equilibrium forming the zwitterion would lie largely to the left. A radical initiator would favor five-membered ring formation via almost concerted addition, as shown in the scheme above. This is based upon a similar mechanism proposed by Butler and Olson.²⁵

CHAPTER II EXPERIMENTAL

General Information

All temperatures are uncorrected and are reported in degrees centigrade; melting points (m.p.) were determined in open capillary tubes using a Thomas-Hoover melting point apparatus. Pressures are expressed as millimeters (mm) of mercury. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, Georgia.

Number average molecular weights (\bar{M}_n) of polymers were determined by vapor pressure osmometry (VPO) on a Wescan Model 230 Recording Vapor Pressure Osmometer Apparatus.

All preparative separations were performed with an Altex Model 332 programmable gradient system fitted with a constant wavelength ultraviolet (UV) detector (254 nanometer (nm)). A Lobar B 24 inch column (E. Merck) with 40-63 μ LiChroprep Si60 Silica gel was used. The solvent used was hexane with rinsing of the column done with 4:1 to 3:1 methylene chloride:methanol.

Infrared spectra (IR) were recorded on a Perkin-Elmer 281 infrared spectrophotometer. Spectra of liquids were obtained neat as a smear on sodium chloride plates, and those of solids were obtained as KBr pellets. Vibrational transition frequencies are reported in wavenumbers (cm^{-1}) using the 1601 cm^{-1} line of a polystyrene film as a standard. The intensity of the bands were assigned the following

classifications: weak (w), medium (m), shoulder (sh), strong (s), broad (br).

. Proton nuclear magnetic resonance (NMR) spectra (60 MHz) were recorded on a Varian EM-360L spectrometer. Carbon-13 (^{13}C) (25.0 MHz) and 100 MHz proton NMR spectra were obtained on a JEOL JNM-FX-100 instrument. Chemical shifts are given in parts per million (ppm) on a δ -scale downfield from tetramethyl silane (TMS) or solvent peaks as internal references (int ref) (chloroform- d (CDCl_3) ^{13}C = 77.0; benzene- d_6 (ϕ - d_6) ^{13}C = 128.0 dimethyl sulfoxide- d_6 ($\text{DMSO}-d_6$) ^{13}C = 39.5).²⁸

Multiplicities of proton and off-resonance decoupled carbon-13 resonances are designated as singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), multiplet (m) or broad (br).

Ultraviolet spectra were measured with a Perkin-Elmer 330 spectrophotometer.

Analytical gas chromatography was done on a open-column capillary HP 5880A series gas chromatograph.

Gel permeation chromatography (GPC) was done on a Waters M 6000A high pressure liquid chromatograph pump with polystyrene-divinylbenzene (TSK gel) columns (i.e., the TSK gel G3000H and G4000H coupled with a guard column attached initially) made by TOYO SODA.

Reagents and Solvents

Reagents were obtained from Aldrich Chemical Co., Eastman Kodak Co., Fisher Scientific Co. or Mallinkrodt Inc. unless otherwise noted. Deuterated NMR solvents were obtained from Merck and Co. and

Aldrich Chemical Co. All gaseous reagents were obtained from Matheson Co. Nickel carbonyl was obtained from Strem Chemicals.

All solvents used for general application were of reagent grade or ACS grade quality. For special purposes, purification of solvents was carried out by following procedures reported in the literature.²⁹

Thus, dimethyl sulfoxide was allowed to stand over barium oxide overnight and was distilled over the barium oxide under reduced pressure; benzene was purified by washing with H_2SO_4 (100 mL/liter) until darkening was slight. 2-Phenylallyl alcohol was obtained in the pure form by precipitating any polymer formed on the reagent's standing, and distilling the alcohol at 95°-97° C/1.5 mm. The literature reported boiling point was (lit b.p.)³⁰ 116°-118° C/11 mm. 2,2'-Azobisisobutyronitrile was recrystallized twice from methanol.

Synthesis of Monomers

2-Chloroallyl 2'-Phenylallyl Ether (1)

The procedure followed for the synthesis of such compounds by Baucom³¹ was generally used. To a flame dried, three necked, 100 mL, round bottomed flask fitted with a dropping funnel through which a constant flow of nitrogen was maintained, was added 1.80 g of 60% sodium hydride (1.08 g, 0.045 mole) in a mineral oil dispersion. The mineral oil was removed by washing with n-pentane (3x10 mLs). The pentane was added, the mixture stirred with a magnetic stirrer and then allowed to stand. The NaH separated out and the pentane and mineral oil drawn off with a disposable pipette. After three

repetitions 20 mLs of dry dimethylsulfoxide (DMSO) was added. 2-Phenylallyl alcohol (5.65 g, 0.042 mole) in 10 mLs of DMSO was added through the dropping funnel slowly. Stirring was continued for four hours (hrs) at room temperature (R.T.). This was then transferred to the dropping funnel and 10 mLs of DMSO and 2-chloroallyl chloride (4.66 g, 0.042 mole) was added to the flask. The alkoxide in the dropping funnel was then added slowly with stirring so that the temperature did not rise appreciably. Stirring was continued for twelve hours. Then water (10 mLs) was added to destroy the excess sodium hydride and the ether was extracted with pentane (3x75 mLs). The pentane extracts were combined and dried over magnesium sulfate. The ether was recovered after the pentane was drawn off on a rotary evaporator and purified by preparative high pressure liquid chromatography.

One and four-tenth grams (16% yield) of the ether (1) was obtained. Gas chromatography showed it to be 97% pure.

^1H NMR (CDCl_3 -TMS) δ : 4.072 (q,2H), 4.406 (m,2H), 5.353 (q,2H), 5.442 (m,1H), 5.550 (m,1H), 7.262-7.438 (br,m,5H). Note: The coupling constants in all of the above multiplets were < 1 Hz.

^{13}C NMR (CDCl_3 -TMS, int ref CDCl_3) δ : 143.62, 138.41, 138.02, 128.32, 127.78, 125.98, 114.72, 113.36, 72.08.

IR (NaCl): 3080 (m), 3060 (m), 3030 (m), 2860 (s), 1635 (s), 1600 (w), 1570 (w), 1490 (s), 1440 (s,br), 1380 (m), 1365 (m), 1315 (sh,w), 1265 (m), 1245 (m), 1175 (s), 1120 (s), 1080 (s,br), 1035 (s), 960 (m), 900 (s), 780 (s), 700 (s), 635 (s).

Elemental analysis: found (calculated) % C 68.72 (69.01), % H 6.29 (6.05), % Cl 17.03 (16.72).

Ethyl α -(Bromomethyl) Acrylate (2)

The method of K. Ramarajan et al.³² was followed. In a nitrogen flushed, three necked, 100 mL, round bottomed flask equipped with a magnetic stirrer. Dean-Stark trap and condenser were placed α -(bromomethyl) acrylic acid (10 g, 0.0595 mole) and thiophene free benzene (75 mLs). Approximately 10 mLs of a binary azeotrope of benzene and water was distilled. The Dean-Stark trap was removed and absolute ethanol (purified by boiling commercial absolute alcohol over magnesium turnings for 4 hrs in a nitrogen atmosphere) (25 mLs) and concentrated sulfuric acid (0.2 mLs) were added slowly. The contents of the flask were boiled in a nitrogen atmosphere for 36 hrs, the condensate being passed through 24 g of molecular sieves (Linde 3A) before being returned to the flask. About 30 mLs of a mixture of benzene and ethanol were removed from the reaction mixture by distillation (at 67° C). Then benzene (25 mLs) was added and another 30 mLs of benzene-ethanol mixture distilled (65-75° C). The residue was poured into water (50 mLs) and neutralized with solid sodium bicarbonate (ca. 4.8 g) until CO₂ evolution ceased. The resulting solution was extracted with three 25 mL portions of ether and the combined extracts dried over anhydrous sodium sulfate for 3 hrs. The ether was removed under reduced pressure on a rotary evaporator and the crude-ester distilled to give a fraction at 39-40° C (0.9 mm) weighing 8.2 g (72% yield). lit b.p.³² 39-40° C (0.9 mm)

^1H NMR (CDCl_3 -TMS) δ : 1.26-1.40 (t, 3H), 4.16-4.38 (q, 2H), 4.19 (s, 2H), 5.96 (s, 1H), 6.32 (s, 1H).

^{13}C NMR (CDCl_3 -TMS, int ref CDCl_3) δ : 13.99, 61.11, 68.41, 125.01, 137.58, 165.75.

IR (NaCl): 2980 (s), 2930 (m), 2870 (m), 1725 (s), 1635 (m), 1445 (m, br), 1380 (m, br), 1310 (m), 1330 (m), 1270 (m), 1225 (m), 1185 (s), 1105 (s), 1025 (m), 950 (s), 900 (w), 875 (w), 855 (w), 810 (m), 720 (m), 680 (m).

2-Phenylallyl 2'-Carboethoxyallyl Ether (3)

The procedure followed by Baucom³¹ was used. To a flame dried, three necked, 100 mL, round bottomed flask, fitted with a dropping funnel through which a constant flow of nitrogen was maintained, was added 0.642 g of 60% NaH (0.385 g, 0.0161 mole) in a mineral oil dispersion. The mineral oil was removed by washing with n-pentane (3x10 mLs). The pentane was added, the mixture stirred with a magnetic stirrer and then allowed to stand. The NaH separated out and the pentane-mineral oil mixture drawn off with a disposable pipette. After three repetitions, 20 mLs of dry DMSO was added. 2-Phenylallyl alcohol (2.152 g, 0.0161 mole) in 10 mLs DMSO was added through the dropping funnel slowly. Stirring was continued for four hours at room temperature. The contents of the flask were then transferred to the dropping funnel and 10 mLs of dry DMSO containing 2-carboethoxyallyl bromide (3.104 g, 0.0161 mole) was added to the flask. The alkoxide (dark purple in color) in the dropping funnel was then added slowly with stirring so that the temperature did not rise appreciably. Stirring was then continued for 12 hrs. Then

water (10 mLs) was added to destroy the excess sodium hydride and the ether was extracted with pentane (3x75 mLs). The pentane fractions were then combined and dried over magnesium sulfate. The ether was recovered after the pentane had been removed under reduced pressure on a rotary evaporator. It was purified by preparative high pressure liquid chromatography. Ether (3)(0.80 g, 20% yield) was obtained.

^1H NMR (CDCl_3 -TMS) δ : 1.217-1.360 (t, 3H, $J=7.2$ Hertz (Hz)), 4.176-4.272 (q, 2H, $J=6.47$ Hz), 4.249 (s, 2H), 4.433 (t, 2H, $J<1$ Hz), 5.366 (q, 1H, $J<1$ Hz), 5.534 (t, 1H, $J<1$ Hz), 5.857 (q, 1H, $J<1$ Hz), 6.280 (m, 1H, $J<1$ Hz), 7.256-7.445 (m, 5H).

^{13}C NMR (benzene- d_6 , int ref pd^6) δ : 14.11, 60.45, 68.54, 72.78, 113.96, 124.83, 126.44, 128.54, 128.68, 138.23, 139.21, 144.67, 165.53.

IR (NaCl): 3060 (w), 2980 (s), 2930 (m), 2900 (m), 2870 (m), 1720 (s), 1635 (m,br), 1600 (w), 1495 (m), 1445 (s), 1380 (s,br), 1305 (s), 1270 (s), 1175 (s), 1155 (s), 1120 (s), 1095 (s), 1035 (s), 950 (m), 910 (m), 860 (w), 815 (w), 780 (s), 695 (s).

Elemental analysis: found (calculated): % C 72.96 (73.17), % H 7.33 (7.32).

Chloroacetone Cyanohydrin (4)

The procedure followed by Ferris and Marks³³ was used. To a solution of sodium bisulfite (62.4 g, 0.6 mole) in water (160 mLs) was added dropwise chloroacetone (46.2 g, 0.5 mole) in a three necked, 2 L, round bottomed flask fitted with a thermometer, mechanical stirrer and dropping funnel. The addition was controlled in order to keep the temperature below 35° C. When all the

chloroacetone had been added, the temperature was cooled to about 25° C and 200 mLs of ethyl ether was added. Then a solution of sodium cyanide (29.4 g, 0.6 mole) in water (80 mLs) was added dropwise at 25-30° C with vigorous mechanical stirring. When all the cyanide solution had been added, the ether layer was separated immediately and the aqueous layer extracted with ethyl ether (2x100 mLs). The combined ether solutions were dried over magnesium sulfate. The crude cyanohydrin was recovered after the ether had been removed under reduced pressure on a rotary evaporator. Cyanohydrin (44.5 g, 74.2% yield)(4) was recovered by distillation b.p. 73-75° C/1.5 mm (lit b.p.³³ 73-74° C/1.5 mm).

¹H NMR (CDCl₃-TMS) δ: 1.708 (s,3H), 3.681 (s,2H), 4.309 (s,1H).

¹³C NMR (CDCl₃-TMS, int ref CDCl₃) δ: 24.80, 50.05, 68.72, 119.50.

IR (NaCl): 3400 (s,br), 3000 (m), 2970 (m), 2945 (m), 2250 (m), 1450 (s), 1430 (s), 1380 (s,br), 1280 (m), 1245 (s), 1150 (s,br), 1080 (s), 960 (s), 870 (s), 770 (s), 730 (w), 695 (m), 685 (m).

Chloroacetone Cyanohydrin Acetate (5)

The procedure followed by Ferris and Marks³³ was used. To a three necked, 250 mL, round bottomed flask fitted with a thermometer, a dropping funnel and a drying tube was added chloroacetone cyanohydrin (4) (44.5 g, 0.372 mole) and 1 mL of concentrated sulfuric acid. To this was added dropwise at 60-70° C with vigorous stirring, acetic anhydride (41 g, 0.40 mole) through the dropping funnel. When all the anhydride had been added, the mixture was stirred for 30 minutes (mins) and then poured into ice water (600

mLs). The resulting mixture was neutralized with solid sodium bicarbonate and extracted with ethyl ether (3x100 mLs). The combined extracts were then dried over magnesium sulfate and the ether finally removed under reduced pressure on a rotary evaporator. Chloroacetone cyanohydrin acetate (5)(32.4 g, 54% yield) was obtained after distillation at 57-59° C/0.3 mm (lit b.p.³³ 57-59° C/0.3 mm).

¹H NMR (CDCl₃-TMS) δ: 1.85 (s,3H), 2.15 (s,3H), 3.90 (s,2H).

¹³C NMR (CDCl₃-TMS, int ref CDCl₃) δ: 20.61, 22.76, 46.83, 70.62, 116.38, 168.38.

α-(Chloromethyl)acrylonitrile (6)

This was obtained by the method used by Ferris and Marks.³³ The apparatus used is shown in Figure 3. The tube at 250° C was primarily to vaporize the chloroacetone cyanohydrin acetate. Chloroacetone cyanohydrin acetate (120 g, 0.743 mole) was dropped at the rate of 1 drop/5 seconds. The condenser was used in case the columns did get blocked up. The product, a brown oil, was poured into water (500 mL) and was neutralized with solid sodium bicarbonate. This was then extracted with ethyl ether (3x200 mLs), the combined portions dried over magnesium sulfate and the ether taken off under reduced pressure on a rotary evaporator. The residue was then fractionally distilled with a Vigreux condenser and the fraction at 75-85°/40 mm collected. This portion (35 g) consisted of 60% α-(chloromethyl) acrylonitrile (6) and 40% of cis- and trans-β-chloro-α-methacrylonitrile (7). The percentages were obtained from the integration in the proton NMR (Fig. 4).

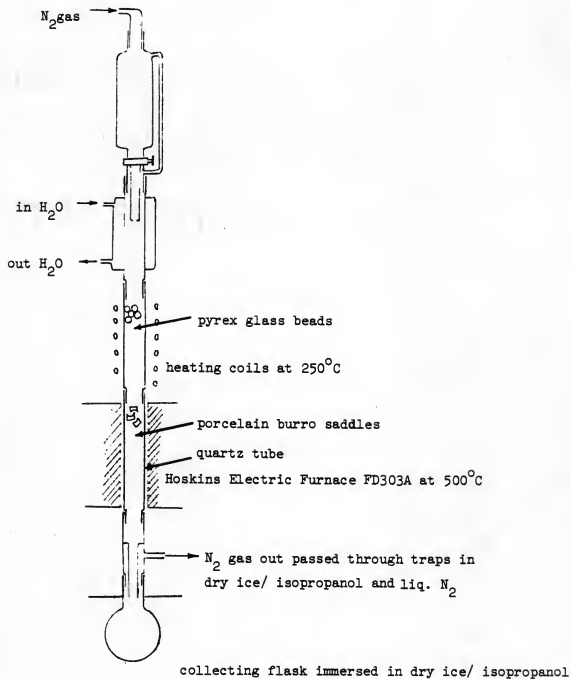


Fig. 3: Apparatus for the pyrolysis of chloroacetone cyanohydrin acetate.

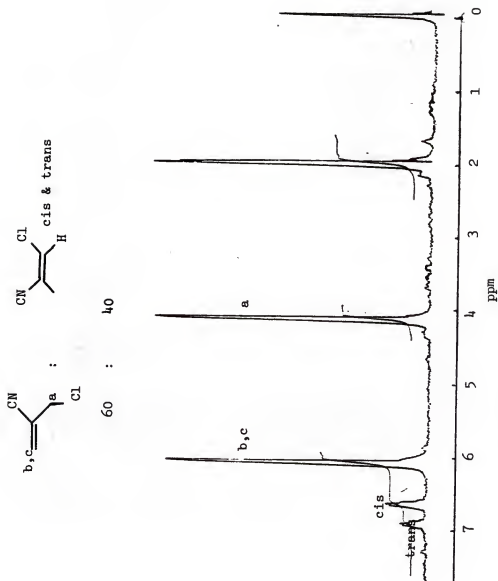


Fig. 4: Proton spectrum of the pyrolysis products with the integration (in CDCl_3)

Lit b.p.³³ of cis- β -chloro- α -methacrylonitrile 57.5-58°/20 mm, trans- β -chloro- α -methacrylonitrile 47-48°/40 mm, α -(chloromethyl) acrylonitrile 61.5-62.5°/18 mm.

¹H NMR (CDCl₃-TMS) δ (6): 4.160 (m, 2H, J<1 Hz), 6.116 (m, 2H, J<1 Hz); (7) cis: 2.018 (s, 3H), 6.666 (q, 1H, J<1 Hz); (7) trans: 2.034 (s, 3H), 6.926 (m, 1H, J<1 Hz).

¹³C NMR (CDCl₃-TMS, int ref CDCl₃) δ (6): 43.23, 113.26, 115.65, 133.29; (7) cis: 18.42, 116.23, 119.79, 131.78; (7) trans: 15.45, 116.23, 119.79, 135.14.

IR (NaCl): 3080 (s), 2960 (m), 2930 (w), 2225 (s), 1750 (w, br), 1605 (s), 1440 (s), 1400 (m), 1380 (w), 1305 (w), 1270 (m), 1220 (w), 1160 (w), 1025 (s), 960 (s), 850 (s), 775 (s), 710 (s).

2-Phenylallyl 2'-Cyanoallyl Ether (8)

The method employed by Baucom³¹ for the synthesis of such compounds was used. To a flame dried, three necked, 100 mL, round bottomed flask fitted with a dropping funnel and through which a constant flow of nitrogen was maintained was added 0.780 g of 60% NaH (0.473 g, 0.0197 mole) in a mineral oil dispersion. The mineral oil was removed with pentane in the manner described in the synthesis of 2-phenylallyl-2'-chloroallyl ether. Then dry DMSO (25 mLs) was added. Through the dropping funnel was slowly added 2-phenylallyl alcohol (2.640, 0.0197 mole) in dry DMSO (10 mLs) and stirred using a magnetic stirrer at room temperature for 4 hrs. The alkoxide was then transferred to the dropping funnel and was added slowly to 3.33 g of 60% 2-cyanoallyl chloride (2 g, 0.0197 mole) with 40% of (7) in

DMSO (10 mLs) so that the temperature did not rise appreciably. Stirring was continued for 12 hrs. Water (10 mLs) was then added and the ether was extracted with pentane (3x75 mLs). The pentane extracts were combined and dried over magnesium sulfate. The pentane was removed under reduced pressure on a rotary evaporator. The ether was purified by preparative high pressure liquid chromatography (Fig. 5). Compound (8) (0.94 g, 24% yield) was recovered.

^1H NMR (benzene d^6 -TMS) δ : 3.492 (t, 2H), 3.988 (m, 2H), 5.150 (q, 1H), 5.243 (m, 2H), 5.370 (m, 1H), 7.086-7.367 (m, 5H). Note: The coupling constants in all of the above multiplets are < 1 Hz.

^{13}C NMR (CDCl_3 -TMS, int ref CDCl_3) δ : 143.33, 138.21, 131.34, 128.42, 127.98, 126.03, 120.33, 117.02, 115.11, 72.61, 69.96.

IR (NaCl): 3080 (m), 3060 (w), 2925 (m), 2860 (m), 2230 (m), 1750 (w, br), 1630 (m), 1610 (w), 1575 (w), 1495 (m), 1445 (m), 1410 (m), 1305 (w), 1120 (s), 1090 (s), 1025 (m), 950 (s), 915 (s), 850 (w), 780 (s), 710 (s).

Chemical analysis: found (calculated): % C 77.92 (78.35), % H 6.46 (6.58), % N 6.73 (7.03).

Bromoacetone (9)

The procedure used here was one followed by Levene.³⁴ A three necked, 2L, round bottomed flask was fitted with a mechanical stirrer, a reflux condenser and a dropping funnel. To this was added water (800 mLs), acetone (250 mLs) and glacial acetic acid (186 mLs). With stirring, the mixture was heated to about 65° C on an oil bath. Through the dropping funnel, bromine (177 mLs, 3.65 mole) was

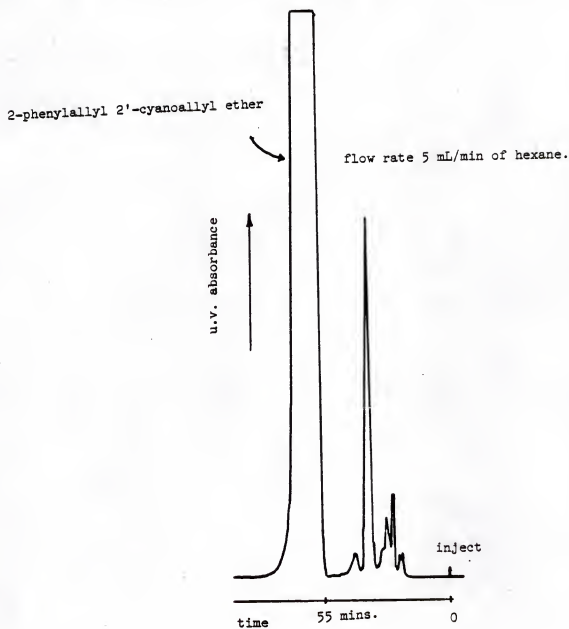


Fig. 5: HPLC chromatograph. Separation of 2-phenylallyl 2'-cyanoallyl ether.

added dropwise, the dropping being regulated by the disappearance of color from the preceding drop. After addition was complete, it was diluted with cold water (400 mLs) cooled in an ice-water mixture and neutralized with solid sodium carbonate (~ 500 g). The oil which separated out was collected and the aqueous layer extracted with ethyl ether (2x400 mLs). The extracts together with the oil was dried over sodium sulfate. The ether was removed by distillation (since bromoacetone is a bad lachrymator, care should be taken accordingly) and not on a rotary evaporator. The residue containing compound (cpd)(9) as well as 1,1-dibromoacetone was distilled and bromoacetone (200 g, 40% yield) was recovered at 86-87°/60 mm. lit b.p.³⁴ 40-42°/13 mm

¹H NMR (CDCl₃-TMS): 3.90 (s,2H), 2.40 (s,3H).

¹³C NMR (CDCl₃-TMS, int ref CDCl₃): 26.98, 34.82, 199.68.

1-Bromo-2,2-dimethoxy Propane (10)

The procedure of Jacobson et al.³⁵ was used for this synthesis. To a 250 mL, round bottomed flask fitted with a drying tube was added 95 mLs of 95% bromoacetone (< 0.5 mole)(5% of 1,1-dibromoacetone), trimethyl orthoformate (60 mLs, 0.55 mole), methanol (25 mLs) and concentrated sulfuric acid (10 drops). After stirring for 2 hrs, the mixture was basified with triethylamine (2 mLs) and then attached to a water pump to remove most of the unreacted methyl formate. The resulting reaction mixture was added to an ice cold solution of sodium hydroxide (20 g) in methanol (200 mLs) destroying the unketalized 1,1-dibromoacetone. This mixture was then partitioned between pentane (300 mLs) and water (200 mLs). The

aqueous layer was extracted with pentane (2x50 mLs) and the three pentane layers combined, washed with water (50 mLs) and dried over potassium carbonate. Removal of the pentane by distillation at atmospheric pressure and distillation under vacuo of residue gave 75 g (0.41 mole > 80% yield) of 1-bromo-2,2-dimethoxypropane boiling at 83° C/80 mm. 1 lit b.p.³⁵ 156° C/760 mm.

¹H NMR (CDCl₃-TMS) δ: 1.45 (s,3H), 3.20 (s,6H), 3.35 (s,2H).

¹³C NMR (CDCl₃-TMS, int ref CDCl₃) δ: 20.61, 34.55, 48.69, 99.76.

IR (NaCl): 2950 (s,br), 2840 (m), 1460 (m), 1425 (m), 1380 (m), 1270 (m), 1250 (m), 1215 (m), 1170 (m), 1165 (m), 1110 (s), 1075 (s), 1045 (s), 925 (w), 880 (m), 830 (m), 745 (m), 675 (m).

Diisopropylethylammonium p-toluenesulfate (11)

The procedure of Jacobson et al.³⁵ was followed. To a 100 mL round bottomed flask was added p-toluenesulfonic acid monohydrate (3.80 g, 0.02 mole) in anhydrous methanol (10 mLs). To this was added diisopropylethylamine (2.80 g, 0.022 mole). The resulting solution was concentrated in vacuo, yielding an oil which crystallized on standing. The solid was crushed and the last traces of solvent removed by subjecting it to vacuo (0.01 mm). Five and five-tenth grams (92% yield) of (11) was obtained of m.p. 85-86° C (lit. m.p.³⁵ 87-88.5° C)

¹H NMR (CDCl₃-TMS): 1.37 (m,15H), 2.35 (s,3H), 2.8-3.3 (m,2H), 3.3-3.9 (m,2H), 7.17 (d,2H), 7.82 (d,2H), 9.18 (br,s,1H).

¹³C NMR (CDCl₃-TMS, int ref CDCl₃): 12.09, 16.86, 18.23, 20.96, 42.40, 53.97, 125.59, 128.27, 139.19, 143.04.

3-Bromo-3-methoxypropane (12)

Method A. The method followed by Hoffman and Greenwood³⁶ was used initially but this method proved laborious. A three necked, 500 mL, round bottomed flask was fitted with a thermometer, a mechanical stirrer and a dropping funnel and to it was added N-bromosuccinimide (50 g, 0.281 mole) in carbontetrachloride (150 mLs). The flask was heated in an oil bath so that the temperature of the mixture was about 55° C. Heating was stopped and 2-methoxypropane (20 mLs) was added. The 2-methoxypropane was initially dried over CaCl_2 and distilled. The addition, with vigorous stirring, was done so that the temperature inside the flask was maintained. After addition was complete, the reaction mixture was cooled to ca. 10° C by immersion in an ice-water mixture. The suspension was filtered to remove the precipitated succinimide and concentrated at the water pump for 15 mins by immersion of the flask in warm water. This removed unreacted 2-methoxypropene, methanol, methyl acetate and some CCl_4 . The remaining solution was washed with potassium hydroxide (2x300 mLs of 1N) and then ice cold water (2x100 mLs). Base destroys 1-bromo-2-methoxy-2-succinimidopropene and bromoacetone. Alkaline conditions also discourages the hydrolysis of any bromoketal to bromoacetone and methanol and suppresses the addition of water to enol ethers. Washing with water neutralizes the solution. The organic layer was dried over CaCl_2 and stirred over Na_2CO_3 . The solution so prepared contains mainly CCl_4 (50%), 2-methoxyallyl bromide (30-35%) and 1-bromo-2-methoxypropene (13) (~ 14%). The percentages were determined by analytical gas chromatography. The carbon tetrachloride was

removed by distillation leaving a yellow residue containing about 55% 2-methoxypropene and 28% 1-bromo-2-methoxypropene with an unidentifiable residue.

Method B. The procedure here was that followed by Jacobson et al.³⁵ This method provided a more stoichiometrically clean product with minimal exposure of the unstable 2-methoxyallyl bromide to room temperature and light.

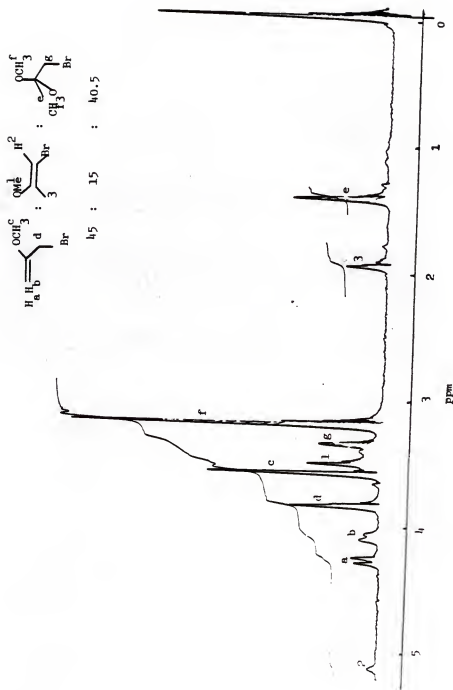
A distillation apparatus with a 100 mL, round bottomed flask containing 1-bromo-2,2-dimethoxypropene (50 g, 0.2732 mole) and diisopropylethylammonium p-toluene sulfonate (1 g) was fitted with a 12 inch, 15 mm diameter vigreux column with heating coils and a short-path distillation assembly. The flask was heated at 150-190° C in an oil bath while distilling of the methanol at the rate of 1 drop/2 seconds. This rate is used so as to keep the complete time of reaction to less than an hour and a half. Complete removal of the methanol was shown by a rise in the head temperature to > 75° C. The fraction collected between temperatures of 85-130° C had the highest percentage (67%) of 2-methoxyallyl bromide. The total fraction (> 85° C) had the following percentages as calculated from the investigation of the proton NMR (Fig. 6):

% 2-methoxyallyl bromide: 45

% 1-bromo-2-methoxy propene (13): 15

% 1-bromo-2,2-dimethoxypropane/starting material): 40.5

¹H NMR (CDCl₃-TMS) δ (12): 4.3 (d,1H), 4.15 (d,1H), 3.9 (s,2H), 3.65 (s,3H); (13): 5.2 (s,br,1H), 3.55 (s,3H), 1.95 (s,3H).

Fig. 6: Proton (60 MHz) spectrum in $CDCl_3$

^{13}C NMR (CDCl_3 -TMS, int ref CDCl_3) δ (12): 31.63, 55.41, 85.29, 159.03; (13): 18.47, 55.02, 77.58, 157.17.

IR (NaCl): 3000 (m), 2950 (m), 1725 (s), 1420 (m), 1390 (m), 1360 (s), 1275 (m), 1240 (m), 1215 (sh,m), 1150 (s), 1005 (w), 700 (w), 660 (w,br).

2-Carboethoxyallyl Alcohol (14)

The procedure of Rosenthal et al.³⁷ was used. Caution: Nickel carbonyl used here is very toxic. Appropriate handling measures were taken. A 2L, five necked, round bottomed flask was equipped with a mechanical stirrer, a thermometer, a dropping funnel, a gas inlet which almost touches the bottom, and a dry ice-cooled condenser. In it was placed 95% ethanol (700 mLs) and the flask was cooled in a dry ice/isopropanol bath. Through the inlet nickel carbonyl was passed with nitrogen as a carrier until the amount of $\text{Ni}(\text{CO})_4$ added (measured by weight difference of the laboratory bottle) was approximately 86 g (0.50 mole). Then was added hydroquinone (10 g) and acetic acid (120 g, 2 mole), and the flask was heated with an oil bath to 55° C with stirring. Through the dropping funnel was added initially 2 g of propargyl alcohol (112 g, 2 mole total) and the color darkened and the internal temperature rose (ca. 2 mins). At this point the heating mantle was removed and the remainder of the propargyl alcohol added dropwise such that the refluxing was under control. The temperature at the end of the addition was 75-80° C. The solution was allowed to stir for 30 mins and then concentrated sulfuric acid (28 mLs, 0.5 mole) was added slowly with stirring via the dropping funnel. Green nickel sulfate hexahydrate

precipitated. The contents were filtered at a water pump through a bromine trap, into a 2 L, round bottomed flask. Concentrated sulfuric acid (10 mLs) was added and the solution was refluxed for 12 hrs, the condensate being passed through a soxhlet-extractor containing anhydrous magnesium sulfate. The reaction solution was then cooled and sodium hydroxide (106 mLs, 5 N) was added to neutralize the acid. An equal volume of water was added and the solution was extracted with chloroform (4x250 mLs). The combined extracts were dried and the chloroform removed under reduced pressure on a rotary evaporator. The liquid residue was distilled to give cpd (14) (93.6 g, 36 % yield) b.p. 55-57° C/0.7 mm. lit b.p.³⁷ 72.5° C/1.5 mm.

¹H NMR (CDCl₃-TMS) δ: 1.3 (t,3H), 2.7 (s,1H), 4.25 (q,2H), 4.3 (s,2H), 5.8 (s,br,1H), 6.25 (s,br,1H).

¹³C NMR (CDCl₃-TMS, int ref CDCl₃) δ: 13.89, 60.58, 61.55, 124.81, 139.58, 166.09.

IR (NaCl): 3440 (s,br), 2980 (s), 2930 (m), 2900 (m), 2870 (w), 1705 (s), 1635 (m), 1445 (m), 1380 (s,br), 1305 (s,br), 1270 (s), 1220 (m), 1170 (s,br), 1095 (m), 1055 (s), 1035 (s,sh), 945 (m), 850 (w), 810 (m).

2-Methoxyallyl 2'-Carboethoxyallyl Ether (15)

The procedure used was similar to the one followed for the synthesis of compound (8). In a flame dried, three necked, 100 mL, round bottomed flask, fitted with a dropping funnel and through which a flow of nitrogen was maintained, was placed 0.8107 g of 60% sodium hydride (0.4864 g, 0.0203 mole) in a mineral oil dispersion. The

mineral oil was removed in the manner described in the synthesis of compound (8). Then dry DMSO (25 mLs) was added. To this was added 2-carboethoxyallyl alcohol (2.634 g, 0.0203 mole) in dry DMSO (10 mLs) very carefully, or else the quick reaction leads to excess foam formation. After a deep red/orange color was observed (2 hours), 5.1 g of 60% 2-methoxyallyl bromide (3.06 g, 0.0203 mole) in dry DMSO (10 mLs) was added dropwise through the dropping funnel. Stirring was continued at room temperature for 12 hrs, water (10 mLs) was added, and the ether extracted with pentane (3x75 mLs). The combined pentane extracts were dried over sodium sulfate and the pentane removed under reduced pressure on a rotary evaporator. The ether (15) (1.01 g, 24.6% yield) was obtained by fractional distillation and was the fraction distilled at 60° C/0.07 mm.

^1H NMR (CDCl_3 -TMS) δ : 1.2 (t,3H), 3.5 (q,2H), 3.55 (s,3H), 4.15 (s,2H), 4.15 (m,2H), 4.55 (s,2H), 5.90 (s,br,1H), 6.24 (s,br,1H).

^{13}C NMR (CDCl_3 -TMS, int ref CDCl_3) δ : 15.11, 55.02, 64.28, 66.28, 68.57, 83.92, 125.93, 137.29, 158.15, 165.36.

IR (NaCl): 2960 (m), 2870 (m,sh), 1715 (s), 1665 (m), 1635 (m), 1450 (m), 1380 (m), 1305 (m), 1255 (m), 1220 (m), 1155 (m), 1100 (s), 950 (m), 880 (m), 820 (m), 740 (w), 680 (m).

Elemental analysis: not done since monomer was unstable, but elemental analysis of polymer was done.

Synthesis of Model Compounds

2-Carobethoxyallyl 2'-Phenylpropyl Ether (16)

The procedure followed here was similar to the one used for the synthesis of compound (15). In a flame-dried, three necked, 100 mL, round bottomed flask fitted with a dropping funnel and through which a flow of nitrogen was kept was placed 0.8187 g of 60% sodium hydride (0.4912 g, 0.02047 mole) in a mineral oil dispersion. The mineral oil was removed in a manner similar to that used for the synthesis of compound (15). Then dry DMSO (25 mLs) was added and through the dropping funnel 2-phenylpropyl alcohol (2.78 g, 0.02047 moles) in dry DMSO (10 mLs) was carefully added dropwise. The resulting solution was stirred magnetically at room temperature for 4 hrs. The alkoxide solution was then transferred to the dropping funnel and added to 2-carboethoxyallyl bromide (3.95 g, 0.02047 moles) in dry DMSO (10 mLs) dropwise such that there was no appreciable rise in temperature. The reaction mixture was allowed to stir for 12 hrs. Water (10 mLs) was added to destroy the unreacted sodium hydride and the ether was extracted with pentane (3x75 mLs). The combined pentane extracts were dried over magnesium sulfate and removed under reduced pressure on a rotary evaporator. The ether (16) (2.03, 40% yield) was recovered by preparative high pressure liquid chromatography (Fig. 7) after distillation at 118° C/0.7 mm.

^1H NMR (CDCl_3 -TMS) δ : 0.936 (t, 3H, $J=7.21$ Hz), 1.221 (d, 3H), 3.320 (d, 2H, $J=3.79$ Hz), 3.212-3.407 (m, 1H), 3.967 (q, 2H), 4.151 (s, br, 2H), 5.7291 (q, 1H, $J<1$ Hz), 6.280 (q, 1H, $J<1$ Hz), 7.117-7.128 (m, 5H).

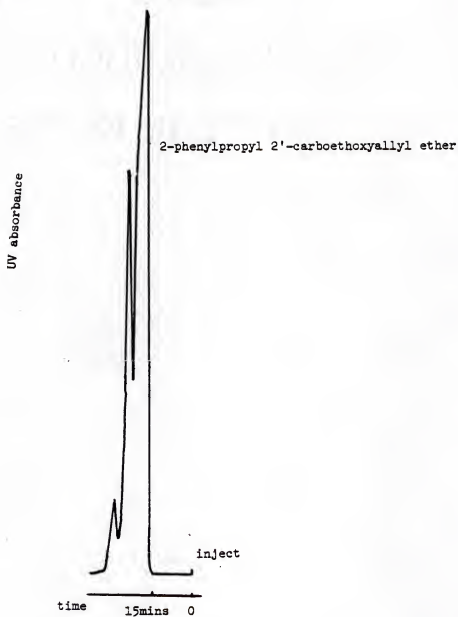


Fig. 7: HPLC chromatograph. Separation of 2-phenylpropyl 2'-Carboethoxyallyl ether.

^{13}C NMR (benzene- d_6 , int ref benzene- d_6) δ : 14.11, 18.39, 40.37, 60.41, 69.37, 76.88, 124.54, 127.71, 128.54, 138.38, 144.67, 165.63.

IR (NaCl): 3030 (m), 2980 (s), 2940 (m), 2900 (m), 2870 (m), 1720 (s), 1640 (m), 1605 (w), 1495 (m), 1455 (m), 1380 (m), 1305 (s), 1270 (s), 1175 (s), 1105 (s), 1025 (m), 950 (m), 860 (w), 820 (w), 760 (m), 700 (s).

Elemental analysis: found (calculated) % C 72.80 (72.58); % H 7.84 (8.06).

2-Phenylpropyl 2'-Cyanoallyl Ether (17)

The procedure followed was similar to that used for the synthesis of compound (16). In a flame dried, three necked, 100 mL, round bottomed flask fitted with a dropping funnel, and through which a flow of nitrogen was maintained, was placed 1.1034 g of 60% sodium hydride (0.6621 g, 0.02759 moles) in a mineral oil dispersion. The mineral oil was removed in the manner described in the synthesis of compound (16). To this was then added dry DMSO (25 mLs) and then 2-phenylpropyl alcohol (3.752 g, 0.02759 moles) in dry DMSO (10 mLs) dropwise through the dropping funnel such that excessive foaming was avoided. The reaction mixture was stirred magnetically for 4 hrs and then transferred to the addition funnel. Then 4.67 g of 60% 2-cyanoallyl chloride (2.8 g, 0.02759 moles) (other 40% being cis and trans- β -chloro- α -methacrylonitrile) in dry DMSO (10 mLs) was placed in the flask and the alkoxide added dropwise such that the temperature did not rise appreciably. Stirring was continued for 4 hrs at the end of which the unreacted sodium hydride was destroyed

with water (10 mLs) and the ether (17) extracted with pentane (3x75 mLs). The pentane extracts were combined and dried over magnesium sulfate and the pentane removed under reduced pressure on a rotary evaporator. The ether (17) (2.49 g, 45% yield) was purified by preparative high pressure liquid chromatography.

^1H NMR (CDCl_3 -TMS) δ : 1.30 (d,3H), 3.10 (p,1H), 3.55 (d,2H), 4.10 (s,2H), 5.90 (s,1H), 6.0 (s,1H), 7.30 (s,5H).

^{13}C NMR (CDCl_3 -TMS, int ref CDCl_3) δ : 18.03, 39.91, 70.23, 76.76, 117.11, 120.47, 126.52, 127.25, 128.37, 131.00, 143.77.

IR (NaCl): 3030 (m), 2965 (m), 2930 (m,sh), 2870 (m), 2225 (m), 1640 (w), 1605 (m), 1495 (m), 1450 (s), 1410 (w), 1390 (w), 1375 (w), 1110 (s), 1025 (w), 1015 (w), 950 (m), 660 (m), 700 (s).

Chemical analysis: found (calculated): % C 77.22 (77.61); % H 7.21 (7.46) % N 7.12 (6.97).

α -Methoxypropionic Acid (18)

The procedure followed here was that used by Leggetter and Brown³⁸ and Reeve and Saddle³⁹ who followed the method of Fuson and Wojcik⁴⁰ for the preparation of ethoxyacetic acid. In a three necked, 1000 mL, round bottomed flask fitted with a condenser and a dropping funnel was placed methanol (300 mLs). Through the condenser was added metallic sodium (0.652 g atoms) cut into bits, such that the solution refluxed gently. Then 2-chloropropionic acid (46.9 g, 0.326 moles) in methanol (40 mLs) was added through the dropping funnel such that the mixture refluxed gently. After the acid was added, the solution was heated for 30 mins so that refluxing

continued. The excess alcohol was then removed by distillation initially and finally by passing steam into the residue. The aqueous solution was cooled and concentrated hydrochloric acid (30.4 mLs) was added. The precipitated sodium chloride was removed by filtration and washed with ethyl ether (2x25 mLs). The original filtrate was saturated with dry sodium sulfate and was then extracted with the ether which was used for washing the precipitate together with additional (2x25 mLs) ether. The combined ether extracts were dried over sodium sulfate and removed by distillation at atmospheric pressure. The acid (18) (26.9 g, 80% yield) was recovered by distillation under reduced pressure 95-96° C/12 mm. 1 lit b.p.³⁸ 108-110°/30 mm

¹H NMR (CDCl₃-TMS) δ: 1.50 (d,3H), 3.45 (s,3H), 4.0 (q,1H), 10.85 (s,1H).

¹³C NMR (CDCl₃-TMS, int ref CDCl₃) δ: 17.93, 57.60, 75.83, 178.37.

Methyl α-Methoxypropionate (19)

The procedure used was that used by Fuson and Wojcik⁴⁰ for the synthesis of ethyl ethoxyacetate. In a three necked, 250 mL, round bottomed flask fitted for a gas inlet and an outlet to a sodium hydroxide solution (5N) was placed α-methoxypropionic acid (23 g, 0.2233 moles) and methanol (50 mLs). The solution was stirred with a magnetic stirrer bar and hydrogen chloride gas was passed into the solution via the inlet, which dipped into the solution, for 5 hrs. The flask was cooled with an ice-water mixture since heat is evolved. It was then allowed to stand for 24 hrs to ensure

completion of the reaction at room temperature. The solution was cooled, and a saturated solution of sodium carbonate added slowly to avoid excessive foaming until the mixture was faintly alkaline to litmus. The ester (19) was extracted with ethyl ether (4x100 mLs) and the extracts combined and dried over anhydrous potassium carbonate. The ether was then distilled at atmospheric pressure and the ester (19) (16.2 g, 62% yield) recovered at 140-142° C/760 mm. 1 lit b.p.³⁹ 142° C/760 mm.

¹H NMR (CDCl₃-TMS) δ : 1.45 (d,3H), 3.40 (s,3H), 3.78 (s,3H), 3.85 (m,1H).

¹³C NMR (CDCl₃-TMS, int ref CDCl₃) δ : 18.32, 51.85, 57.60, 76.32, 173.50.

2-Methoxy Propanol (20)

The method employed here was that used by Reeve and Saddle³⁹ and adapted from the method of Fickett, Garner and Lucas⁴¹ for the reduction of α -chloropropionyl chloride and Moffett's⁴² method for the reduction of α -(1-pyrrolidyl)propionate. In a three necked, 500 mL, round bottomed flask fitted with a reflux condenser, mechanical stirrer with a mercury seal and dropping funnel was placed lithium aluminum hydride (9.1742 g, 0.2412 moles) and dry ethyl ether (200 mLs). The mixture was refluxed for 3 hrs to effect solution. To this was added methyl α -methoxypropionate (46.75 g, 0.3962 mole) in dry ethyl ether (100 mLs), at first a few drops until a white precipitate appeared and after cooling the solution down to 0° C with an ice-water mixture, the remainder. The addition was completed in 20 mins and stirring was continued for 30 mins. The excess

LiAlH_4 was decomposed by adding methyl acetate (21.5 mLs) slowly with stirring. This was followed by the addition of hydrochloric acid (258 mLs, 6N). The aqueous layer was separated, made strongly alkaline with sodium hydroxide (430 mLs, 6N) and the alcohol extracted with ethyl ether (2x250 mLs). The original ether layer together with the extracts were combined and dried over anhydrous potassium carbonate. The ethyl ether was removed by distillation at atmospheric pressure and the alcohol (20) (37.4 g, 58% yield) recovered by distillation of the residue at 133-135° C/760 mm. 1t b.p.³⁹ 135° C/760 mm.

^1H NMR (CDCl_3 -TMS) δ : 1.117 (d,3H), 2.621 (s,1H), 3.388 (s,3H), 3.494 (d,2H), 3.49 (m,1H).

^{13}C NMR (CDCl_3 -TMS, int ref CDCl_3) δ : 15.11, 56.24, 65.94, 77.39.

IR (NaCl): 3400 (m,br), 2970 (m), 2930 (m,br), 2820 (m), 1630 (w,br), 1450 (m), 1370 (m), 1350 (m), 1235 (m), 1190 (m), 1140 (s), 1080 (s), 1040 (s,sh), 980 (m), 890 (m), 825 (w), 800 (m).

2-Methoxypropyl 2'-Carboethoxyallyl Ether (21)

The procedure followed was similar to that followed for the synthesis of compound (17). In a flame dried, three necked, 100 mL, round bottomed flask, fitted with a dropping funnel and through which a flow of nitrogen was maintained, was placed 0.7047 g of 60% sodium hydride (0.4228 g; 0.0176 moles) in a mineral oil dispersion. The mineral oil was removed in a manner described in the procedure for the synthesis of compound (17). Dry DMSO (25 mLs) was added and stirred with a magnetic stirrer bar. To this was carefully added

dropwise 2-methoxypropanol (1.58 g, 0.0176 moles) in dry DMSO (10 mLs). Stirring was continued for 4 hrs. The alkoxide solution was then transferred to the dropping funnel and in the flask was placed 2-carboethoxyallyl bromide (3.4 g, 0.0176 moles) in dry DMSO (10 mLs). The alkoxide solution was added dropwise such that the temperature did not change appreciably. Stirring was continued for 12 hrs. Water (10 mLs) was added to destroy the unreacted NaH. The ether (21) was then extracted with pentane (3x75 mLs) and the combined extracts dried over magnesium sulfate. The pentane was then removed under reduced pressure on a rotary evaporator and the ether (21) (1.78, 50%) was recovered by distillation at 55° C/0.06 mm.

^1H NMR (CDCl_3 -TMS) δ : 1.159 (d,3H), 1.304 (t,3H), 3.397 (s,3H), 3.478 (d,2H), 3.353-3.489 (m,1M), 4.234 (s,2H), 4.226 (q,2H), 5.885 (q,1H, $J < 1$ Hz), 6.298 (m,1H, $J < 1$ Hz).

^{13}C NMR (CDCl_3 -TMS, int ref CDCl_3) δ : 14.08, 16.37, 56.68, 60.53, 69.35, 74.47, 75.78, 125.30, 137.34.

IR (NaCl): 2970 (m), 2920 (m), 2895 (m,sh), 2860 (m,sh), 1710 (s), 1630 (w), 1450 (m), 1370 (m), 1300 (s), 1365 (s), 1170 (s), 1150 (s), 1100 (s), 1020 (m), 945 (m), 850 (w), 810 (m), 680 (w).

Elemental analysis: found (calculated): % C 59.03 (59.41); % H 8.96 (8.91).

Miscellaneous Reactions2-Chloro-2-propenyl Acetate⁴³ (22)

2,3-Dichloropropene (16.679 g, 0.1503 moles), sodium acetate (15.428 g, 0.188 mole), glacial acetic acid (8 mLs) and pyridine (0.5 mLs) were put into a tube and sealed. The tube was heated in an oil bath at 140-150° C for 12 hrs. It was then opened after cooling and the contents of the tube extracted with ether (3x100 mLs). The combined extracts of ether were then washed with dil. sulfuric acid (100 mLs, 10%) and then a saturated solution of sodium bicarbonate (100 mLs). The extracts were dried overnight over magnesium sulfate. The ether removed under reduced pressure on a rotary evaporator and the ester (22) distilled at 142-147° C. 11.1 b.p.⁴³ (143-145° C) (11.1 g, 55% yield).

¹H NMR (CDCl₃-TMS) δ: 2.126 (s,3H), 4.651 (s,2H), 5.412 (s,1H), 5.441 (s,1H).

¹³C NMR (CDCl₃-TMS, int ref CDCl₃) δ: 20.52, 65.84, 114.72, 135.83, 169.89.

2-Chloro-2-propenol (23)⁴³

2-Chloro-2-propenylacetate (22) (28.4 g, 0.21 moles) and methanol (35.5 mLs) containing 1% HCl was refluxed in a 100 mL round bottomed flask for twelve hours. The methanol was distilled off. The solution was then poured into water (100 mLs) and sodium bicarbonate (1.1 g) added to neutralize the acid. The alcohol was extracted with ether (3x100 mLs) and the combined ether extracts dried over magnesium sulfate. The ether was removed under reduced

pressure on a rotary evaporator and the alcohol (23) distilled at 135-137° C (lit b.p.⁴³ 130° C) (15.2 g, 78% yield)

¹H NMR (CDCl₃-TMS) δ: 3.25 (s,1H, exch. with D₂O), 4.15 (s,2H), 5.35 (s,1H), 5.50 (s,1H).

¹³C NMR (CDCl₃-TMS, int ref CDCl₃) δ: 65.5, 111.9, 140.6.

2-Chloroallyl Ether (24)

The procedure followed was similar to that followed for the synthesis of compound (21). In a flame dried, three necked, 100 mL, round bottomed flask fitted with a dropping funnel through which a flow of nitrogen was maintained, was placed 0.8107 g of 60% sodium hydride (0.4864 g, 0.02027 moles) in a mineral oil dispersion. The mineral oil was removed in a manner described in the procedure for the synthesis of compound (8). Dry DMSO (25 mLs) was added and stirred with a magnetic stirrer bar. To this was added 2-chloroallyl alcohol (23) (2.249 g, 0.0243 moles) in DMSO (10 mLs) carefully dropwise. Stirring was continued for 4 hrs. The alkoxide solution was then transferred to the dropping funnel and in the flask was placed 2,3-dichloropropene (2.70 g, 0.024 moles) in DMSO (10 mLs). The alkoxide solution was added dropwise such that the temperature did not change appreciably. Stirring was continued for 12 hrs. Water (10 mLs) was added and the ether (24) was extracted with pentane (3x75 mLs) and the combined extracts dried over magnesium sulfate. The pentane was removed under reduced pressure on a rotary evaporator and the ether (24) (1.2 g, 36% yield) recovered by preparative high pressure liquid chromatography.

^1H NMR (CDCl_3 -TMS) δ : 4.12 (s,4H), 5.42 (s,2H), 5.52 (m,2H).

^{13}C NMR (CDCl_3 -TMS, int ref CDCl_3) δ : 72.42, 113.80, 137.48.

IR (NaCl): 2860 (w), 1635 (m), 1440 (w), 1385 (w), 1365 (w), 1255 (w), 1270 (w), 1180 (m), 1090 (s), 1035 (w), 890 (s), 720 (m), 640 (m).

Elemental analysis: found (calculated): % C 43.51 (43.11); % Cl 41.92 (42.51); % H 4.85 (4.80).

Ethyl- α -(bis-2-chloroallyl)-malonate (25)

The method of Hill and Fischer⁴⁴ was used. In a three necked, 250 mL, round bottomed flask, fitted with a mechanical stirrer, a dropping funnel and a condenser was placed ethanol (75 mLs). To it was added sodium (4.2 g, 0.1826 gr. atom) slowly to keep the mixture refluxing gently. After the sodium was dissolved diethylmalonate (29 g, 0.183 mole) was added dropwise through the dropping funnel. Stirring was continued for an hour and then 2,3-dichloropropene (44.4 g, 0.4 mole) was added and stirring continued for 12 hrs at room temperature. The sodium chloride which precipitated was filtered off and the ethanol removed under reduced pressure on a rotary evaporator. Water (40 mLs) was added and compound (24) extracted with ether (4x50 mLs). The combined ether extracts were dried over magnesium sulfate. The ether was removed under reduced pressure on a rotary evaporator and compound (24) (34.4 g, 61% yield) distilled at 107° C/0.75 mm.

^1H NMR (CDCl_3 -TMS) δ : 1.266 (t,6H), 3.16 (s,4H), 4.22 (q,4H), 5.343 (br,s,4H).

^{13}C NMR (CDCl_3 -TMS, int ref CDCl_3) δ : 13.74, 40.52, 55.31, 61.79, 117.74, 136.90, 169.50.

Synthesis of Polymers

Polymerization of 2-Chloroallyl 2'-Phenylallyl Ether

2-Chloroallyl 2'-Phenylallyl ether (1) (0.926 g, 0.0044 moles) with benzene (1.389 g) and 2,2'-Azobisisobutyronitrile (AIBN) (0.046 g, 5% w/w of monomer) were divided equally and put into two polymerization tubes and taken through five freeze-thaw cycles on a mercury diffusion vacuum line for degassing, and sealed. These were then immersed, with shaking, in a water bath at 40° C and an oil bath at 60° C, respectively.

The tubes were opened after 4 days and poured into methanol (2x100 mLs). There was no precipitation. On evaporation of the methanol and benzene, the monomer (1) was recovered. The proton NMR did not show any new peaks and the integration ratios were maintained as in the monomer.

Polymerization of 2-Carboethoxyallyl 2'-Phenylallyl Ether

2-Carboethylallyl 2'-Phenylallyl ether (3) (1.036 g, 0.0042 moles), benzene (1.554 g) and AIBN (0.0518 g, 5% w/w of monomer) were divided equally and put into two polymerization tubes and taken through five freeze-thaw cycles on a mercury-diffusion vacuum line. These were then immersed, with shaking, in an oil bath at 60° C and a water bath at 40° C. After 4 days, the tubes were opened and the polymer precipitated into methanol (2x100 mLs). The yields were as follows:

40° C polymerization: 0.292 (56%)

60° C polymerization: 0.441 g (85%)

The polymers were soluble in DMSO, benzene, dimethylformamide, acetone, chloroform.

40° C polymerization sample:

^1H NMR (CDCl_3 -TMS) δ : 0.95, 1.24, 2.1, 3.0, 4.1, 7.1 (Fig. 20).

^{13}C NMR (CDCl_3 -TMS, int ref CDCl_3) δ : 13.35-14.10, 26.34-28.58, 40.30, 41.62, 44.71, 51.17, 60.72, 72.66, 126.03-128.32, 140.41-144.99, 173.55-174.96 (Fig. 21).

IR (KBr): 2980 (m), 2850 (m), 1730 (s), 1630 (w), 1600 (w), 1580 (w), 1495 (m), 1470 (m), 1445 (m), 1380 (m), 1245 (m), 1200 (m), 1110 (s), 1025 (m), 965 (w), 890 (w), 850 (w), 760 (m), 695 (m).

60° C polymerization:

^1H NMR (CDCl_3 -TMS) δ : 0.95, 1.24, 1.625, 2.1, 3.0, 4.1, 7.1 (Fig. 15 of Discussion and Results).

^{13}C NMR (CDCl_3 -TMS, int ref CDCl_3) δ : 13.35-14.10, 30.16, 40.60, 41.72, 44.84, 50.20, 60.72, 72.37, 126.03-128.37, 140.65-143.97, 173.69.

IR (KBr) same as for polymer formed at 40° C.

VPO (benzil standard): 6550.

Elemental analysis: found (calculated): % C 71.07 (73.17); % H 7.33 (7.32).

Polymerization of 2-Cyanoallyl 2'-Phenylallyl Ether at 40%

2-Cyanoallyl 2'-Phenylallyl ether (8) (1.09 g, 0.0055 mole), benzene (1.635 g) and AIBN (0.0545, 5% w/w of monomer) were divided equally and placed in two polymerization tubes and taken through five

freeze-thaw cycles on a mercury diffusion vacuum line for degassing, and sealed. They were then immersed with shaking, in an oil bath at 60° C and a water bath at 40° C, respectively. The tube in the 60° C bath developed a white precipitate within 30 mins and was removed after 2 hrs and the polymer was precipitated into methanol (100 mLs). The tube at 40° C developed a precipitate in about 2 hrs and the polymer was precipitated into methanol (100 mLs) after 6 hrs. The polymers in both cases were insoluble in DMSO, benzene dimethylformamide, acetone, and chloroform. The percentage conversions in the two cases were as follows: 40° C polymerization 0.32 g (59%); 60° C polymerization 0.37 g (68%).

IR (similar for both cases except for relative intensities) (KBr): 3040 (m), 3020 (m), 2910 (m), 2850 (m), 2225 (w), 1625 (w), 1600 (w), 1580 (w), 1490 (m), 1465 (m), 1445 (m), 1380 (m), 1240 (m), 1095 (s), 960 (m), 885 (w), 835 (w), 760 (m), 695 (s).

Elemental analysis: found (calculated): % C 75.24 (78.35); % H 6.46 (6.58), % N 6.73 (7.03).

Polymerization of 2-Cyanoallyl 2'-Phenylallyl Ether at 10%

2-Cyanoallyl 2'-Phenylallyl ether (8) (1.08 g, 0.0054 moles), benzene (9.81 g) and AIBN (0.0545 g, 5% w/w of monomer) were divided equally into three polymer tubes and taken through five freeze-thaw cycles on a mercury diffusion vacuum line for degassing and sealed. They were then immersed, with shaking, in a water bath at R.T. for 5 days, a water bath at 40° C for 8 hrs and a water bath at 60° C for 1 hr. The conversion was kept low in all three cases. The polymers formed in the three cases were precipitated in methanol (3x100 mLs).

The percent yields were as follows:

polymerization at R.T.: 0.092 g (26%)

polymerization at 40° C: 0.078 g (22%)

polymerization at 60° C: 0.05 g (14%)

The polymers were soluble in DMSO, dimethyl formamide, acetone and chloroform.

The IR spectra were similar to the polymers formed in the previous experiment done at 40% monomer concentration.

Polymer sample formed at R.T.:

^1H NMR (CDCl_3 -TMS) δ : 1.2574, 1.5638, 3.0627 (br), 4.1204, 4.4428, 5.3620, 5.5240, 6.0263, 7.33.

Polymer sample formed at 40° C:

^1H NMR (CDCl_3 -TMS) δ : 1.258, 1.724, 2.315 (br), 3.126 (br), 3.917, 4.120, 4.442, 5.350, 5.576, 6.020, 7.334.

Polymer sample formed at 60° C:

^1H NMR (CDCl_3 -TMS) δ : 1.257, 1.547, 1.725, 2.317, 3.100, 3.924, 4.133, 4.40, 5.366, 5.54, 6.023, 7.334.

Polymerization of 2-Carboethoxyallyl 2'-Methoxyallyl Ether

2-Carboethoxyallyl 2'-Methoxyallyl ether (15) (0.553 g, 0.0028 moles), benzene (0.8295 g) and AIBN (0.0277 g, 5% w/w of monomers) were placed in a polymerization tube and taken through five freeze-thaw cycles on a mercury diffusion vacuum line for degassing and sealed. This was then immersed, with shaking, in a water bath at 40° for 2 days. The polymer was precipitated in methanol (100 mLs). A similar procedure was followed for 0.475 g (0.0024 moles) of cpd

(15), benzene (0.7125 g) and AIBN (0.0238 g, 5% w/w of monomer). The water bath was however at 60° C.

The percentage yields were as follows:

polymer formed at 40° C: 0.45 g (81%)

polymer formed at 60° C: 0.39 g (82%)

Both polymer samples were soluble in benzene, chloroform, acetone, DMSO and DMF.

Sample formed at 40° C:

^1H NMR (CDCl_3 -TMS) δ : 1.152, 1.349 (sh), 1.862, 2.261, 3.222, 3.557, 4.081, 4.265.

^{13}C NMR (CDCl_3 -TMS, int ref CDCl_3) δ : 14.96, 20.27, 27.19, 42.30 (br), 481.69, 49.51, 54.73, 65.74, 83.04, 99.47, 173.65.

IR (KBr): 2970 (m), 2940 (m), 2870 (m), 1725 (s), 1670 (w), 1635 (w), 1445 (w), 1375 (m), 1300 (w), 1230 (w), 1100 (s), 845 (w), 810 (w), 745 (w).

Elemental analysis: found (calculated): % C 57.36 (59.96); % H 7.88 (8.06).

Sample polymerized at 60° C:

^1H NMR (CDCl_3 -TMS) δ : 1.133, 1.340, 1.873, 2.171, 3.218, 3.560, 4.081, 4.250.

^{13}C NMR (CDCl_3 -TMS, int ref CDCl_3) δ : 15.01, 20.37, 27.19, 48.25, 49.17, 54.78, 66.28, 83.04, 99.47, 173.65.

IR (KBr): same as 40°C polymerization sample.

Attempted Polymerization of 2-Chloroallyl Ether

2-Chloroallyl ether (0.98 g, 0.0059 moles), benzene (1.47 g) and AIBN (0.049 g, 5% of monomer) were placed in a polymer tube. It was taken through five freeze-thaw cycles on a mercury diffusion vacuum line and sealed. It was then immersed in a water bath at 60° C for 4 days. The contents were then poured into methanol (100 mLs) but no precipitate was obtained. A viscous liquid was obtained after removing the methanol but was not identified.

CHAPTER III RESULTS AND DISCUSSION

NMR Analyses

The assignments of unsaturated carbons have been rationalized using the resonance structures as shown in Figure 8.⁴⁵ As shown in the top resonance structure with an electron releasing group, a negative charge in one of the contributing resonance structure would shift the carbon β to the methoxy group to a lower δ value and, along the same arguments, the carbon α to the methoxy group to a higher δ value. Similarly an electron withdrawing group would lower electron density on the carbon β to the electron withdrawing group as shown in the bottom resonance structure of the above mentioned figure. This analysis has been used in conclusions regarding "charge transfer" or a biased electron delocalization in related structures.

A similar analysis could be drawn up for assigning hydrogens in the proton NMR.

Synthesis of Monomers

The Williamson reaction^{46a} was the base reaction in the synthesis of the four monomers. The reaction is depicted in general terms below.

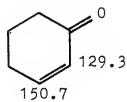
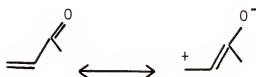
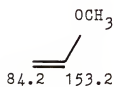
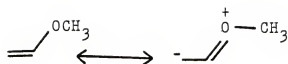
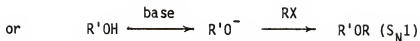
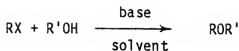
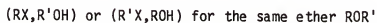


Fig. 8: Information regarding C 13 NMR chemical shifts of substituted alkenes.



Hence for each ether the following combination of reactants could be used.



For the monomers synthesized the ease of synthesis of the halide and the corresponding alcohol dictated the combination used.

For the allylic ethers prepared, whenever the unsaturated point had an electron-withdrawing group attached in the halide, the alkoxide in DMSO was added to the halide in DMSO and whenever the unsaturation point had an electron donating group attached in the halide, it (in a DMSO solution) was added to the alkoxide. This was due to the possible attack of the alkoxide as shown.



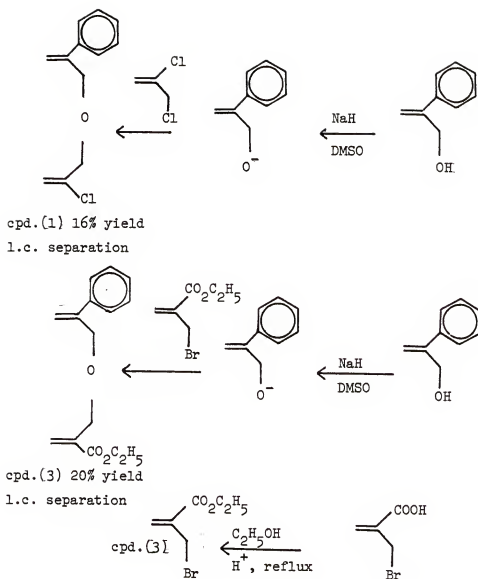
giving side reactions thereby

2-Phenylallyl 2'-Chloroallyl Ether (1)

(Scheme 3) The combination used here for the Williamson reaction was 2-phenylallyl alcohol⁴⁷ and 2-chloroallyl chloride due to the availability of both reagents. The 2-phenylallyl alkoxide formed by sodium hydride was added to 2-chloroallyl chloride. The product, 2-phenylallyl 2'-chloroallyl ether (1), was isolated by high pressure liquid chromatography since an attempt at fractional distillation did not give a very efficient separation from the unreacted 2-phenylallyl alcohol. The 2-phenylallyl 2'-chloroallyl ether structure was confirmed via proton NMR and carbon-13 NMR (as shown in Fig. 9), IR and elemental analysis. The assignments were confirmed by an INEPT⁴⁸ spectrum which showed negative peaks at $\delta = 72.077$, 113.058 and 114.722 ppm. The assignments for carbon 1 and carbon 3 were done on the basis of electron density at the double bond itself and on the analysis discussed at the beginning of this chapter. The infrared spectra showed peaks at 1635 and 1600 cm^{-1} corresponding to the C=C stretch of the α -phenyl allyl and 2-chloroallyl moiety respectively.

The proton assignments were based on general assignment principles as well as integration ratios.

As can be seen, the two sets of unsaturated carbons do not differ widely as regards electron density as can be concluded from Figure 9 and the initial analysis.



Scheme 3: Synthesis of compounds (1) and (3).

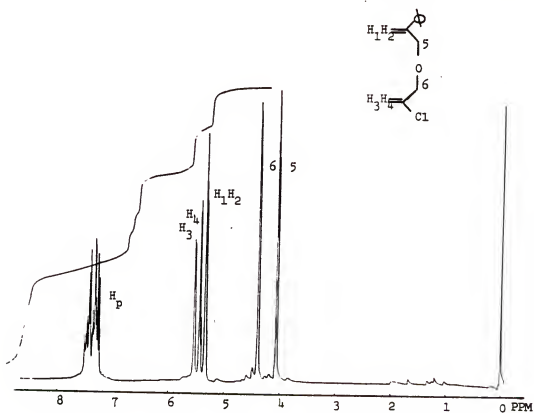
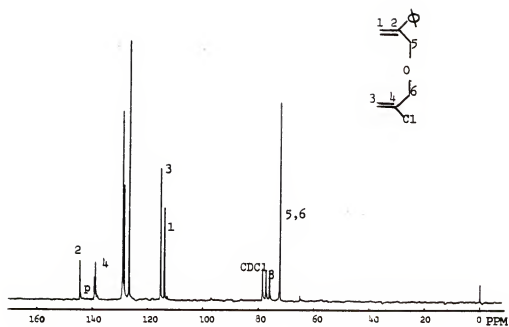


Fig. 9: Proton (100 MHz) spectrum and noise decoupled C 13 spectrum of compound (1) in CDCl₃.

2-Carboethoxyallyl 2'-Phenylallyl Ether (3)

(Scheme 3) The combination used in the synthesis was 2-phenylallyl alcohol and 2-carboethoxyallyl bromide (2). The 2-carboethoxyallyl bromide (2) was synthesized via the acid catalyzed esterification as reported³² from α -(bromomethyl)acrylic acid. The structure of (2) was confirmed by C 13 NMR, proton NMR and IR. The C 13 NMR and proton NMR assignments are listed in Table 1. Here again 2-phenylallyl alkoxide in DMSO was added to the 2-carboethoxyallyl bromide as described.³¹ The monomer was isolated via preparative high pressure liquid chromatography since attempts to isolate the compound (3) via distillation under reduced pressure (upto 0.5 mm) seemed to polymerize it. The identity of the monomer was confirmed via carbon-13 and proton NMR spectra which are shown in Figure 10. The carbon assignments were confirmed by an INEPT spectrum showing negative peaks at $\delta = 69.04, 73.28, 114.46$ and 125.33 ppm and positive peaks at $\delta = 14.61$ and 60.95 ppm. The proton NMR spectrum showed four different peaks assigned as shown. The two sets of carbons do differ to a greater extent than in compound (1) as can be seen from the carbon spectra. The C=C stretch for the 2-phenylallyl and the 2-carboethoxyallyl moiety occur at 1635 and 1600 cm^{-1} in the IR spectra.

2-Phenylallyl 2'-Cyanoallyl Ether (8)

(Scheme 4) The mechanism of the first step would be

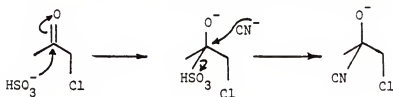
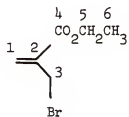
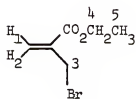


Table 1: Carbon-13 and proton NMR assignments for compound (2)



proton δ :	1.26-1.40	5
(CDCl ₃)	4.16-4.38	4
	4.19	3
	5.96	1
	6.32	2

carbon δ :	13.99	6
(CDCl ₃)	61.11	5
	68.41	3
	125.01	1
	137.58	2
	167.75	4

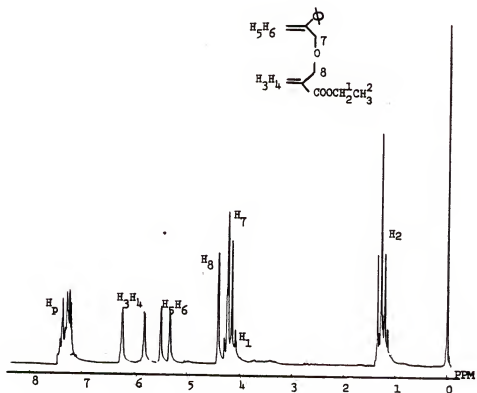
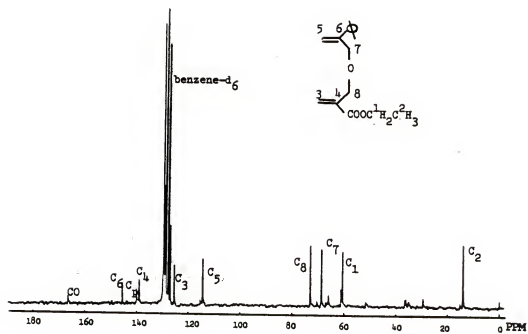
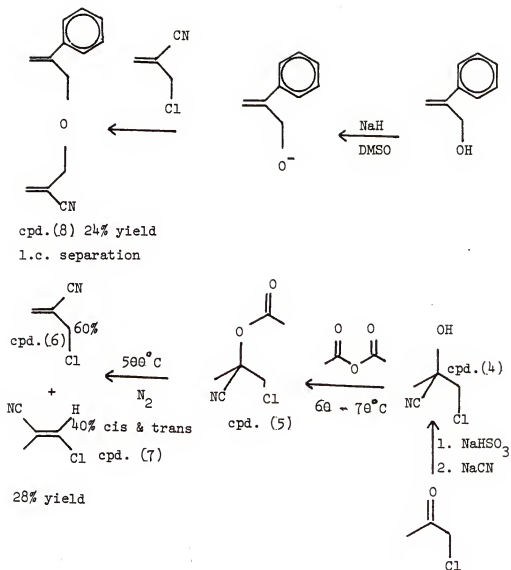


Fig. 10: Proton (100 MHz) spectrum (in CDCl₃) and C 13 noise decoupled 25 MHz spectrum (in benzene-d₆) of compound (3).



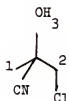
Scheme 4: Synthesis of compound (8).

The identity of the chloroacetone cyanohydrin (4) was confirmed by carbon-13 and proton NMR and IR spectra and the assignments for the protons and carbons shown in Table 2. The chloroacetone cyanohydrin acetate (5) was confirmed by carbon-13 and proton NMR spectra and the assignments for the protons and carbons shown in Table 3.

Compound (4) showed the CN stretch in the IR at 2250 cm^{-1} .

2-Cyanoallyl chloride (6) was confirmed by carbon-13 and proton NMR and IR. The assignments for the protons and carbons are shown in Table 4. In the proton NMR H_1 and H_2 occur at the same chemical shift. They occur at $\delta = 6.09$ and 6.19 in CCl_4 and agree with the literature.⁴⁹ The pyrolysis apparatus used in the synthesis was modified from the one used by M. Tsurushima et al.^{50,51} The mixture of 2-cyanoallyl chloride (6) and β -chloro- α -methacrylonitrile (7) could be used directly since in (7) the chloride is attached to the double bond and could not be eliminated and the difference in rate of elimination of the allylic chloride in (6) to the allylic hydrogen in (7) would be very great. Compound (7) is the first fraction collected during the liquid chromatographic separation of 2-cyanoallyl 2'-phenylallyl ether (8). The C 13 NMR and proton NMR assignments for the cis and trans isomer of 7 is listed in Table 5. 2-Cyanoallyl 2'-phenylallyl ether (8) was identified by carbon-13 NMR, proton NMR, IR and elemental analysis, the first two spectra being shown in Figure 11. The INEPT spectrum (Fig. 12) helps identify the different carbons. The two sets of carbons do differ to a

Table 2: Proton and carbon-13 NMR assignments for compound (4).

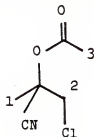


proton δ :	1.708	1
(CDCl ₃)	3.681	2
	4.309	3

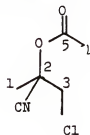


carbon δ :	24.80	1
(CDCl ₃)	50.05	2
	68.72	3
	119.50	C \equiv N

Table 3: Proton and carbon-13 NMR assignments for compound (5).

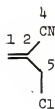
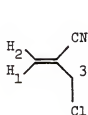


proton δ :	1.85	1
(CDCl ₃)	2.15	3
	3.90	2



carbon δ :	20.61	1
(CDCl ₃)	22.76	4
	46.83	3
	70.62	2
	116.38	CN
	168.38	5

Table 4: Proton and carbon-13 NMR assignments for compound (6).



proton δ : 4.160 3
(CDCl₃) 6.116 1,2

carbon δ : 43.23 3
(CDCl₃) 113.26 2
115.65 4
133.29 1

Table 5: Proton and carbon-13 NMR assignments for compound (7).



proton δ : cis
(CDCl₃) 2.018 1
6.667 2

trans
2.034 1
6.926 2



C-13 δ : cis
(CDCl₃) 18.42 3
116.23 4
119.79 2
131.78 1

trans
15.45 3
116.23 4
119.79 2
135.14 1

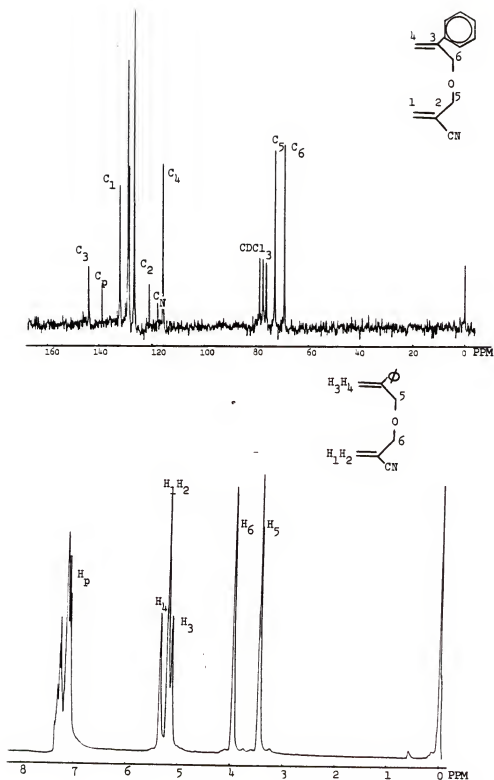


Fig. 11: Proton spectrum (100 MHz) (in benzene d_6) and C 13 noise decoupled spectrum (25 MHz) (in $CDCl_3$) of compound (8).

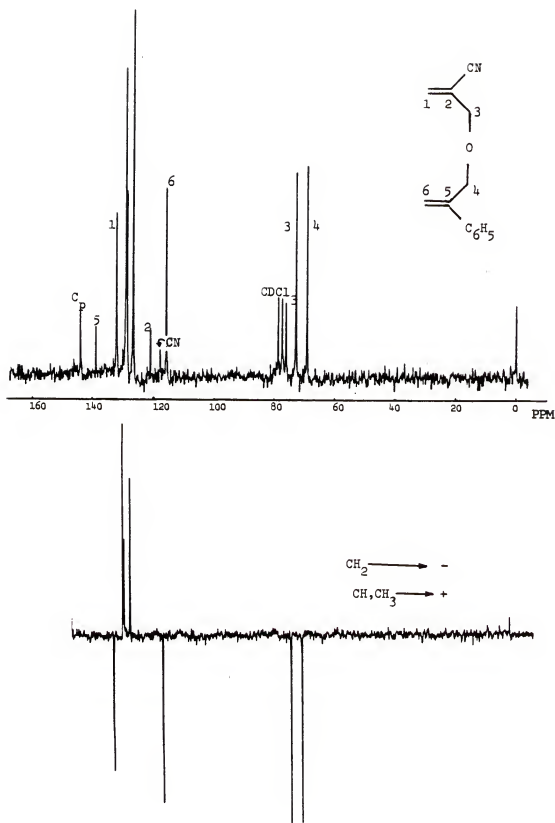
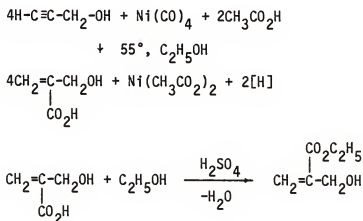


Fig. 12: 25 MHz decoupled and multiplicity determination ^{13}C spectra for compound (8).

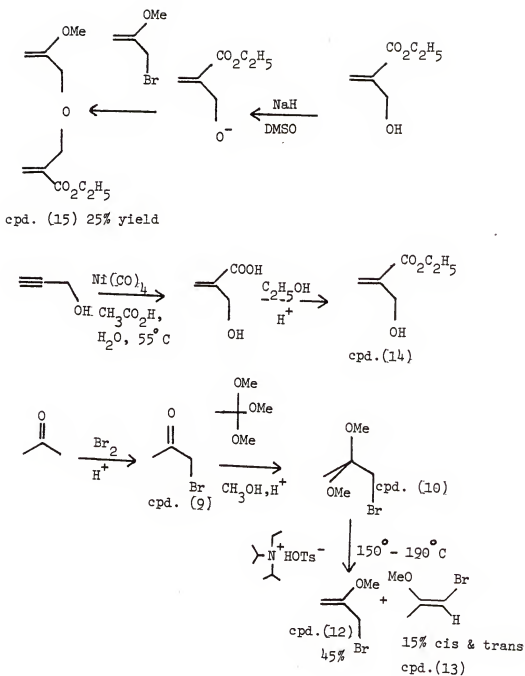
greater extent than even compound (3). The infrared spectrum shows the C≡N stretch at 2230 cm⁻¹.

2-Carboethoxyallyl 2'-Methoxyallyl ether (15)

(Scheme 5) The combination used here for the Williamson reaction was 2-carboethoxyallyl alcohol (14) and 2-methoxyallyl bromide (12). The syntheses of the synthons^{46b} of the other combination were not reported. 2-Carboethoxyallyl alcohol was prepared via the method of Rosenthal et al.³⁷

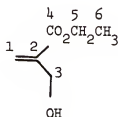
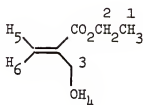


The identity of the ethyl-α-(hydroxymethyl)acrylate (14) was confirmed via C 13 NMR, proton NMR and IR. The assignments for the carbons and protons are listed in Table 6. The first method for the synthesis of 2-methoxyallyl bromide via bromination using N-bromosuccinimide of Greenwood and Hoffman³⁶ was successful but the method of Jacobson et al.³⁵ was preferred. The drawback of the method of Greenwood et al. was that one obtained a carbon tetrachloride solution of the 2-methoxyallyl bromide contaminated with products resulting from the addition of succinimide to the enol



Scheme 5: Synthesis of compound (15).

Table 6: Carbon-13 and proton NMR assignments for compound (14).



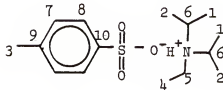
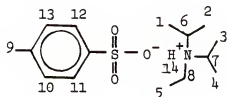
proton δ :	1.3	1	carbon δ :	13.89	6
(CDCl ₃)	2.7	4 (deuterium exchange)	(CDCl ₃)	60.58	5 (or 3)
				61.55	3 (or 5)
	4.25	2		124.88	1
	4.3	3		139.58	2
	5.8	5		166.09	4
	6.25	6			

Table 7: Carbon-13 and proton NMR assignments for compound (9).



proton δ :	2.40	1	carbon δ :	26.98	1
(CDCl ₃)	3.90	2	(CDCl ₃)	34.82	3
				199.68	2

Table 8: Carbon-13 and proton NMR assignments for compound (11).



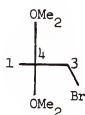
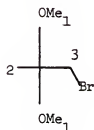
proton δ :	1.37	1,2,3,4,5
(CDCl ₃)	2.35	9
	2.8-3.3	8
	3.3-3.9	6,7
	7.17	10,13
	7.82	11,12
	9.18	14

carbon δ :	12.09	3
(CDCl ₃)	16.86	1
	18.23	2
	20.96	4
	42.39	5
	54.00	6
	125.59	7
	128.27	8
	139.19	9
	143.04	10

ether double bond. It also resulted in only 10-20% conversion to the desired 2-methoxyallyl chloride. The 1-bromo-2,2-dimethoxypropane (10) was prepared from bromoacetone using the method described by Jacobson et al.³⁵ Bromoacetone was synthesized from acetone and the identity was confirmed by carbon-13 NMR, proton NMR, and IR. The assignments for the carbons and protons are listed in Table 7. The catalyst used here was reported to be the most efficient³⁵ and was synthesized as per the method reported by Jacobson et al.³⁵ The structure was confirmed by carbon-13 NMR and proton NMR. The assignments of these are listed in Table 8. 1-Bromo-2,2-dimethoxypropane (10) was confirmed by carbon-13 NMR, proton NMR and IR. The assignments for the carbons and protons are listed in Table 9.

The fraction collected between 85° C and 130° C had the highest percentage of 2-methoxyallyl bromide.¹² This would seem true since 1-bromo-2,2-dimethoxypropane (10), the other major constituent, has a boiling point of 156° C. The proton NMR assignments for (12) and (13) are listed in Figure 6 and the carbon-13 NMR spectrum and the assignments in Figure 13. The mixture could be used directly in the subsequent reaction for the synthesis of (14) since again the allylic bromine in (12) would be more easily displaced than the allylic hydrogen in 1-bromo-2-methoxypropene (13) and the bromine in (10) by 2-carboethoxyallyl alkoxide. 2-Methoxyallyl 2'-carboethoxyallyl ether (14) was prepared using the Williamson reaction and identified using C 13 NMR, proton NMR and IR. The spectra are shown in Figures 14 and 15. Figure 14 also shows the off-resonance decoupled C 13 spectrum. The structure was also confirmed by an INEPT spectrum.

Table 9: Carbon-13 and proton NMR assignments for compound (10).



proton δ :	1.45	2
(CDCl ₃)	3.20	1
	3.35	3

carbon δ :	20.61	1
(CDCl ₃)	34.55	3
	48.69	2
	99.76	4

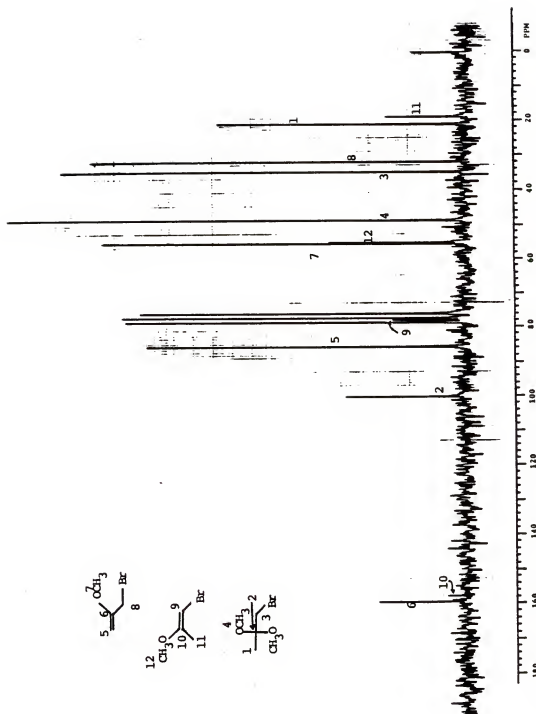


Fig. 13: Carbon-13 (25 MHz) spectrum of the pyrolysis of 1-bromo-2,2-dimethoxypropane

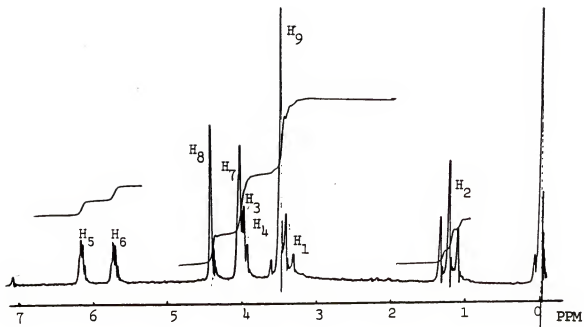
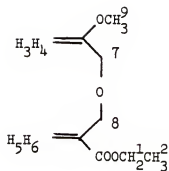


Fig. 14: Proton spectrum (60 MHz) in $CDCl_3$ (15).

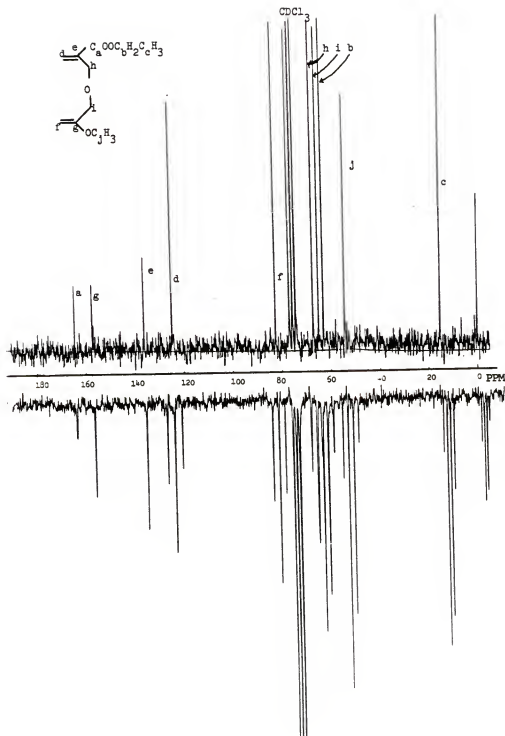


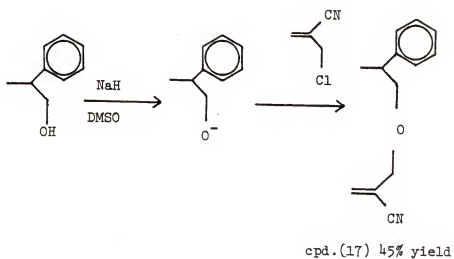
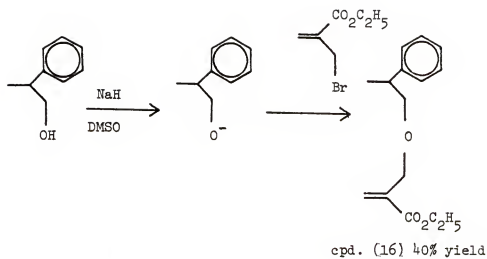
Fig. 15: Noise and off-resonance decoupled C 13 spectra in CDCl_3 (15).

Synthesis of Model Compounds

The model compounds were synthesized mainly to see if there was any charge transfer occurring in the free state of the monomer. Hence compounds were synthesized having structures similar to the monomers prepared. The monomer, 2-chloroallyl 2'-phenylallyl ether, was not pursued since it was not expected to show any "charge transfer" interaction due to its non-polymerizability. The two 2-sets of carbons are comparable as per the carbon-13 NMR spectra. This would be expected since the chlorine group is electron releasing by resonance and electron withdrawing by induction, and field effects which contribution predominates would determine whether the chlorine group acts as an electron donating or an electron withdrawing group. It was decided therefore only to synthesize model compounds for compounds (3), (8) and (15). The model compounds would have an unsaturation point only attached to the electron withdrawing group since if the unsaturation point was attached to the electron releasing group chemical shifts in the proton and carbon-13 NMR spectra would be extremely small.

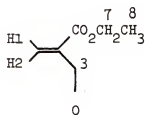
2-Carboethoxyallyl 2'-Phenylpropyl Ether (16)

(Scheme 6) This was prepared by the Williamson reaction using 2-phenyl propanol and 2-carboethoxyallyl bromide (2), with sodium hydride as the base. The identity of the 2-carboethoxyallyl 2'-phenylpropyl ether (16) was confirmed by C 13 NMR, proton NMR, IR and elemental analysis. The C 13 NMR and proton NMR assignments are listed in Table 10.

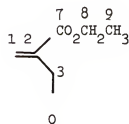


Scheme 6: Synthesis of compounds (16) and (17).

Table 10: Carbon-13 and proton NMR assignments for compound (16).



proton δ :	0.936	8
(CDCl ₃)	1.221	5
	3.320	4
	3.212-3.407	6
	3.967	7
	4.151	3
	5.7291	1
	6.280	2
	7.117-7.128	Hp



carbon δ :	14.11	9
(benzene d ₆)	18.39	6
	40.37	8
	60.41	4
	69.37	3
	76.87	5
	124.54	1
	127.71	Cp
	128.54	Cp
	138.38	2
	144.67	Cp
	165.53	7

An attempt to isolate (16) via distillation proved unsuccessful to purify it totally and preparative high pressure liquid chromatography had to be used.

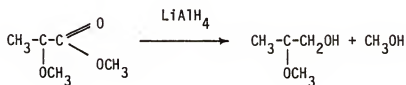
2-Cyanoallyl 2'-Phenylpropyl Ether (17)

(Scheme 6) The Williamson reaction was utilized for this synthesis. The 40:60 mixture of β -chloro- α -methacrylonitrile (7) and α -(chloromethyl)acrylonitrile (6) was used directly and (17) isolated via preparative high pressure liquid chromatography.

The compound (17) was isolated and identified via C 13 NMR, proton NMR, IR and elemental analysis. The C 13 NMR and proton NMR spectra are shown in Figure 16.

2-Carboethoxyallyl 2'-Methoxypropyl Ether (21)

(Scheme 7) The Williamson reaction was used here and the reaction was carried out by adding 2-carboethoxyallyl bromide (2) in DMSO to 2-methoxyprop-oxide in DMSO. 2-Methoxypropanol was synthesized using standard reduction procedures from methyl-2-methoxypropionate with lithium aluminum hydride.



2-Methoxypropanol was identified by C 13 NMR, proton NMR and IR. The assignments for the C 13 NMR and proton NMR spectra are listed in Table 11.

The methyl-2-methoxypropionate (19) was obtained via esterification of 2-methoxypropionic acid (18). The carbon-13 NMR

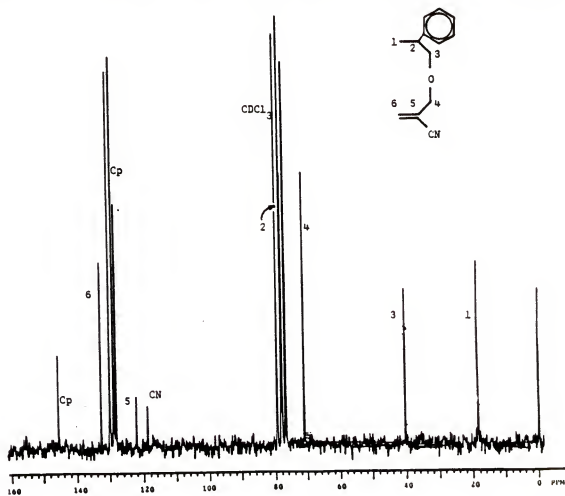
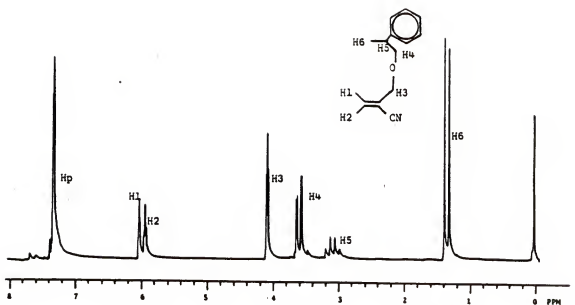
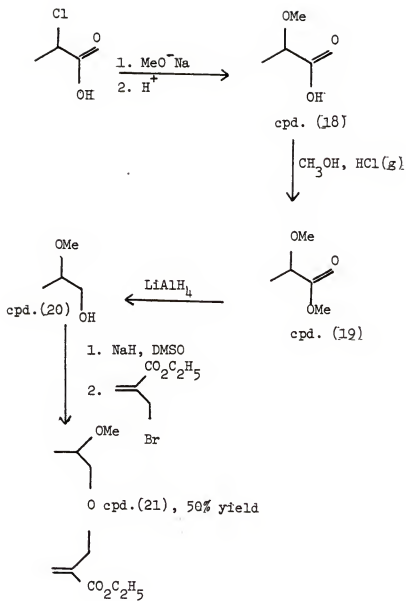
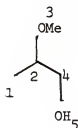


Fig. 16: Proton (100 MHz) NMR spectrum (in CDCl_3) and carbon-13 (25 MHz) NMR spectrum (in CDCl_3) of compound (17).



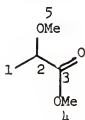
Scheme 7: Synthesis of compound (21).

Table 11: Proton and carbon-13 NMR assignments for compound (20).



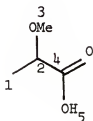
proton δ :	1.117	1	C-13 δ :	15.11	1
(CDCl ₃)	2.621	5 (D ₂ O exchange)	(CDCl ₃)	56.24	3
	3.388	3		65.94	4
	3.494	4		77.39	2
	3.49	2			

Table 12: Proton and carbon-13 NMR assignments for compound (19).



proton δ :	1.45	1	carbon δ :	18.32	1
	3.40	5		51.85	5
	3.78	4		57.60	4
	3.85	2		76.32	2
				173.50	3

Table 13: Proton and carbon-13 NMR assignments for compound (18).

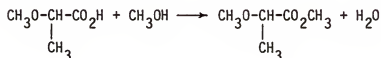
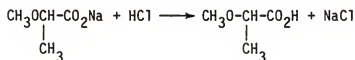
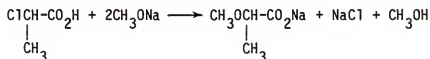


proton δ :	1.50	1
	3.45	3
	4.0	2
	10.85	5

carbon δ :	17.93	1
	57.60	3
	75.83	2
	178.37	4

and proton NMR assignments used for the identification of (18) and (19) are listed in Tables 12 and 13, respectively.

The 2-methoxypropionic acid (18) was obtained via a substitution of the chlorine in 2-chloropropionic acid.⁴⁰



2-Carboethoxyallyl 2'-methoxypropyl ether (21) was purified via distillation. The identity was confirmed via carbon-13 NMR, proton NMR, IR and elemental analysis. The carbon-13 NMR spectrum and the INEPT spectrum with the assignments are shown in Figure 17 and the proton NMR assignments are listed in Table 14.

Comparison of Spectra

The carbon-13 chemical shifts of the unsaturated carbons of interest in compounds (3), (8) and (15) and their respective models (16), (17) and (21) are listed in Tables 15, 16 and 17. The protons for the models have decreased in chemical shift and the carbons have decreased (C_1 to which the protons are attached $< \text{C}_3$) and increased ($\text{C}_2 > \text{C}_4$) in chemical shifts with respect to the monomers. This is

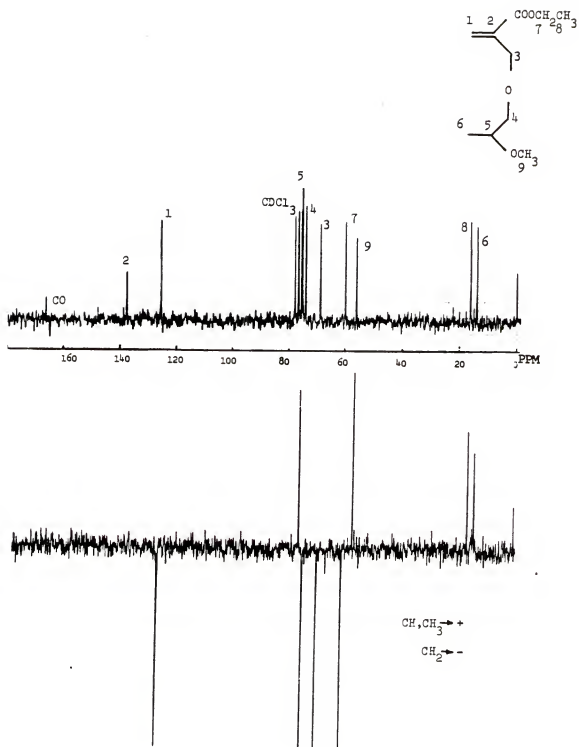
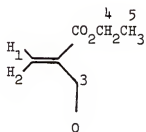


Fig. 17: 25 MHz decoupled and multiplicity determination sequence C 13 spectra (21).

Table 14: Proton NMR assignments for compound (21).



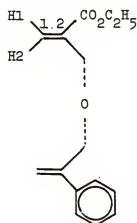
proton δ :	1.159	9
(CDCl_3)	1.304	5
	3.397	7
	3.478	6
	3.353-3.489	8
	4.234	3
	4.226	4
	5.885	1
	6.298	2

consistent in all three pairs. Assuming no intermolecular interaction due to the dilute conditions under which the NMR spectra were obtained, one could conclude that intramolecular interaction amounting to "charge transfer" could be taking place. Referring back to Section A and Figure 8, if there had been no "charge transfer," relative to the molecule with charge transfer the double bond with the electron donating group would be more electron rich which could be looked upon as another very weak electron donating group attached to the unsaturation. This would cause C_1 to increase and C_2 to decrease relative to the molecule having "charge transfer" if the weak electron donating group were attached to C_1 .

A similar analysis could be drawn for the double bond with the electron withdrawing group which would cause C_3 to decrease and C_4 to increase. This latter case is, indeed, what is seen in the case of the monomers and their model compounds. A similar analysis could be drawn for the hydrogens attached to C_1 in Tables 15, 16 and 17. They would decrease in chemical shift as would C_{10} . However, certain deviations may be expected anyway since factors other than "charge transfer" would come into effect because the hydrogens would be susceptible to steric interactions.

The magnitude of the shift in the carbon-13 NMR would be expected to be small as could be derived from an experiment done by mixing 2,4,6-trimethoxystyrene⁵² with fumaronitrile. The scheme for preparation used for the synthesis of 2,4,6-trimethoxystyrene is shown in Figure 19. The proton and carbon-13 NMR chemical shifts of two separate compounds and a mixture in a 1:1 molar ratio are shown

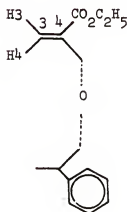
Table 15: Comparative proton and carbon chemical shifts for compounds (3) and (16).



R.T.	benzene- d^6	CDCl_3
H1	6.284	6.302
H2	5.802	5.856
C1	124.83	125.59
C2	138.23	137.34

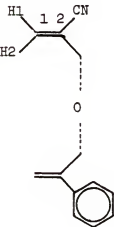
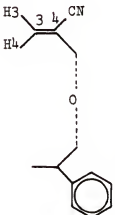
decr.

incr.



R.T.	benzene- d^6	CDCl_3
H3	6.280	5.238
H4	5.729	5.754
C3	124.54	125.15
C4	138.38	137.43

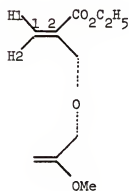
Table 16: Comparative proton and carbon chemical shifts for compounds (8) and (17).

	R.T.	benzene-d ⁶	CDCL ₃
	H1		5.979
	H2	5.243	131.39
	C1	130.19	120.23
	C2	120.79	
	R.T.	benzene-d ⁶	CDCL ₃
	H3	5.242	5.955
	H4	5.170	5.869
	C3	129.80	131.00
	C4	121.03	120.47

decr.

incr.

Table 17: Comparative proton and carbon chemical shifts for compounds (15) and (21).

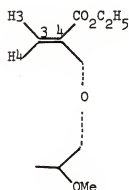


R.T.

benzene-d⁶CDCL₃

H1	6.366
H2	5.841
C1	125.03
C2	138.23

6.346
5.909
125.93
137.29



R.T.

benzene-d⁶CDCL₃

H3	6.327
H4	5.850
C3	124.49
C4	138.48

6.298
5.885
125.30
137.34

decr.

incr.

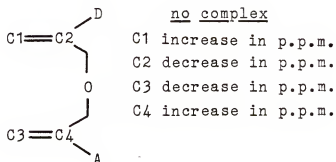
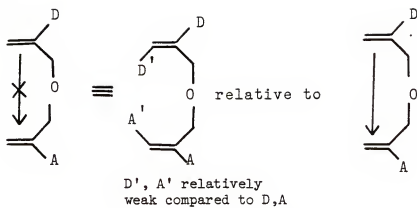
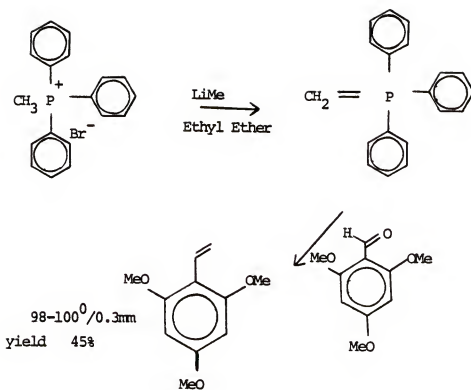
N.M.R

Fig. 18: Analysis for explanation of observed shifts.



compound supplied by Dr. S. Mallakhpour.

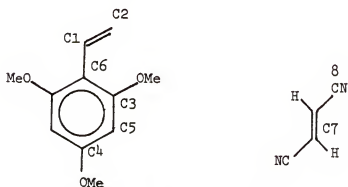
Fig. 19: Synthesis scheme used for 2,4,6-trimethoxystyrene.

in Tables 18 and 19. The shift of the fumaronitrile protons and carbons are effectively in the same range as the shifts in the monomer and model compounds discussed. The shifts in the case of the non-aromatic double bond in 2,4,6-trimethoxystyrene would, as expected, not be very great due to a resonance interaction with the aromatic ring.

The chemical shifts in the case of fumaronitrile would be a decrease on mixing of the components, to a lower δ due to loss of electron density as is seen by R.B. Seymour et al.²⁶ The magnitude of the difference in chemical shift is greater in the case of (8) and (17) than in (3) and (16) in Table 20 which would be expected since CN is a stronger electron withdrawing group (keeping the electron donating group, phenyl the same) than carboethoxy.

A similar magnitude difference is seen in the case of (15) and (21) and (3) and (16) in Table 21 where methoxy is a stronger electron donating group than phenyl and carboethoxy is kept the same. The differences mentioned above are more pronounced in benzene-d₆²³ than in CDCl₃ where the actual conditions of polymerization (with respect to solvent) are kept constant. This might be expected since benzene is a less polar solvent than CDCl₃. Benzene could itself act as an electron donor towards "charge transfer" but the intramolecular complex formed could have a more negative free energy of formation due to both enthalpy as well as entropy factors. The enthalpy factor could be due to the styrene moiety being a better electron donor and the entropy factor could be due to the molecules not being immobilized in the case of

Table 18: Comparative carbon chemical shifts for fumaronitrile and 2,4,6-trimethoxystyrene separate and mixed in a 1:1 molar ratio.



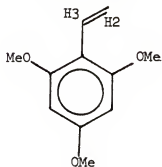
C 13 NMR in benzene- d_6 (ppm)

separate at R.T.

1:1 at R.T.

C1	under the benzene peaks (~ 128)	
C2	116.01	116.06
C3	160.22	160.17
C4	160.75	160.75
C5	91.16	91.11
C6	109.09	109.04
C7	117.77	117.57
C8	114.06	114.06

Table 19: Comparative proton chemical shifts for fumaronitrile and 2,4,6-trimethoxystyrene separate and mixed in a 1:1 molar ratio. H1



Proton NMR in benzene- d^6 (ppm)

	separate at R.T.	1:1 at R.T.
H3	7.593	7.560
	7.471	7.439
	7.413	7.380
	7.291	7.259
H1	6.509	6.485
	6.477	6.454
	6.327	6.305
	6.295	6.273
H2	5.642	5.625
	5.610	5.593
	5.521	5.504
	5.489	5.472
Hf	4.565	4.349

Table 20: ^{13}C chemical shift differences with acceptors different

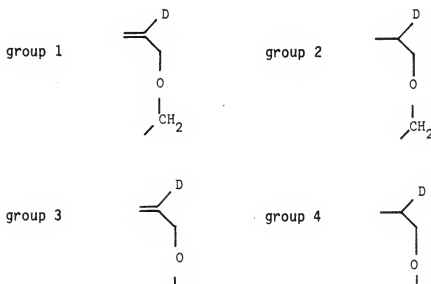
(ϕ const)	difference C_1 & C_3		C_2 & C_4	
	$\phi \text{ d}^6$	CDCl_3	$\phi \text{ d}^6$	CDCl_3
CN	0.39	0.39	-0.24	-0.24
CO_2Et	0.29	0.44	-0.15	-0.10

Table 21: ^{13}C chemical shift differences with donors different

(carboethoxy const)	difference C_1 & C_3		C_2 & C_4	
	$\phi \text{ d}^6$	CDCl_3	$\phi \text{ d}^6$	CDCl_3
ϕ	0.29	0.44	-0.15	-0.10
OCH_3	0.54	0.63	-0.24	-0.05

intramolecular "charge transfer." Benzene however has been quoted to be a nondonor solvent.²³

Referring to Figure 18 and the model compounds if the group 1 were considered a stronger electron releasing group than group 2, the relative effect on the chemical shifts would be that C_3 would decrease and C_4 increase in ppm. This would imply that group 3 is a stronger electron releasing group than group 4 making C_5 appear at a lower ppm than C_6 , which is contradictory to what is observed.



An attempt to investigate the UV spectra with change in temperature led to a decrease in UV intensity with increase in temperature as is shown in Figure 20. This is quite similar to data observed by Butler and Olson²⁵ and does not prove, individually, the existence of an interaction.

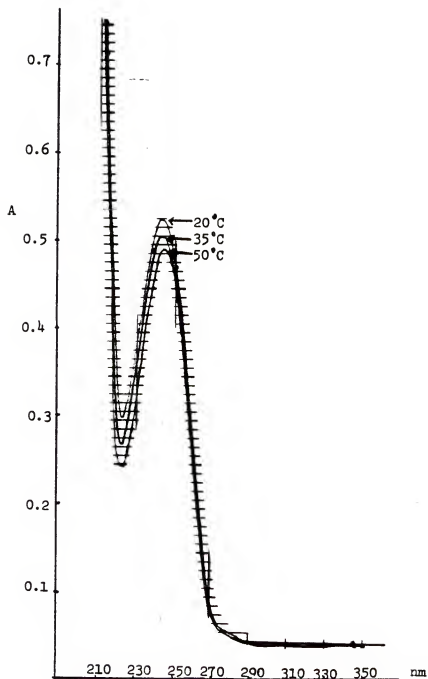


Fig. 20: UV of compound (15) (conc = 10^{-5} M) in t-butyl alcohol at different temperatures.

Polymer Synthesis and Characterization

Poly(2-chlorallyl 2'-phenylallyl ether)

The attempted polymerization of monomer (1) did not afford even oligomers. The monomer was recovered from the attempted polymerization.

Poly(2-carboethoxyallyl 2'-phenylallyl ether)

Poly(2-carboethoxyallyl 2'-phenylallyl ether) was formed at 40° C and 60° C. The polymers formed at the two temperatures were characterized by NMR, IR, elemental analysis and GPC. The number average molecular weight of the polymer formed at 60° C was determined by Vapor Pressure Osmometry to be 6550. The number average molecular weight of the polymer formed at 40° C seemed to be in the same range as per the GPC curve (Fig. 21).

The GPC curve using dimethylformamide (DMF) indicates that the polymer has a very broad molecular weight distribution. The solubility of the polymer in solvents such as benzene, chloroform, acetone, dimethyl formamide and dimethylsulfoxide indicates that the polymer is linear and, hence from the expected structure, cyclic.

The proton NMR and C 13 NMR spectra are shown in Figures 22 and 23. The carbon spectra are nearly identical but the proton NMR spectra with the help of spectra of methyl-4-phenyl butyrate^{53a} and methyl-5-phenylvalerate^{53b} seem to mediate a five-membered ring predominance at 40° C changing to a six-membered predominance at 60° C.

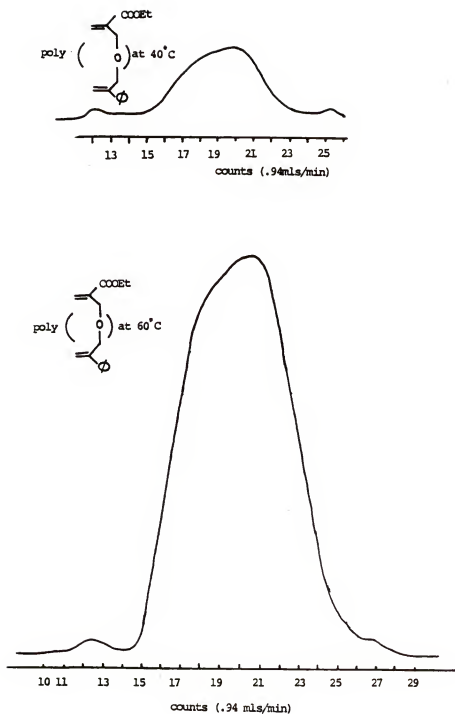


Fig. 21: GPC curves for polymers (in DMF) formed at different temperatures.

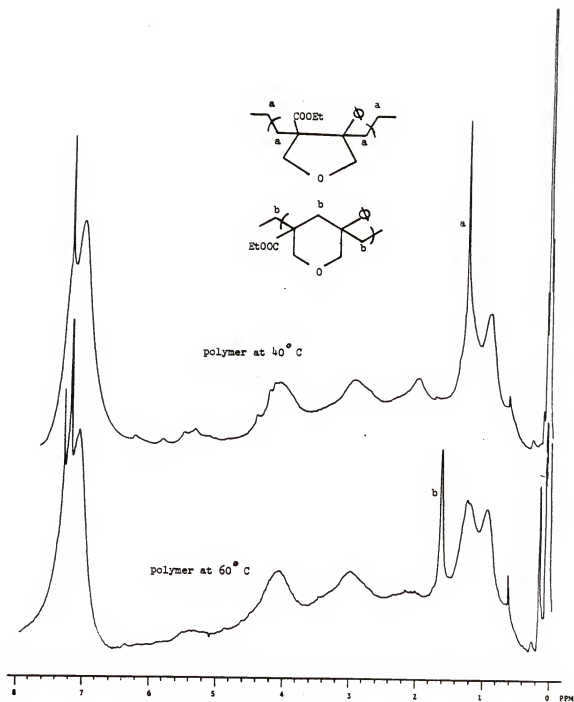


Fig. 22: Proton NMR spectra for polymers (in CDCl_3) formed at 40° C and 60° C.

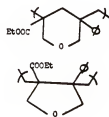
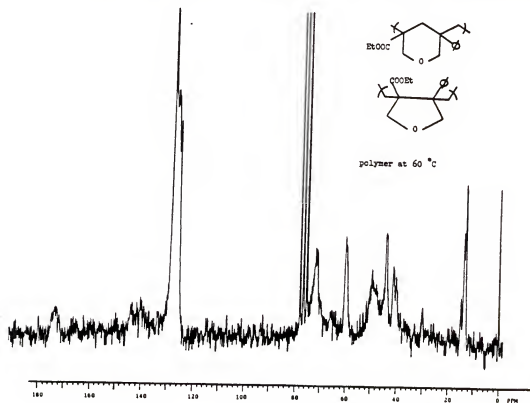
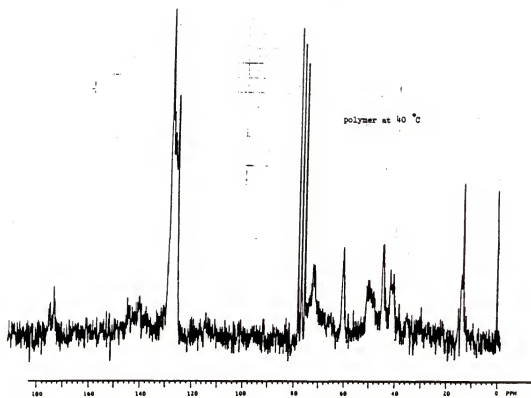


Fig. 23: Carbon-13 NMR spectra for polymers formed at 40° C and 60° C.

Poly(2-cyanoallyl-2'-phenylallyl Ether)

The polymer formed at 40% monomer concentration was extremely insoluble and hence could not be analyzed with respect to NMR spectroscopy. Polymer formed at 10% monomer concentration was soluble in chloroform, DMF, acetone and DMSO and GPC curves (Fig. 24) showed these to be bimodal. The area under the curve from counts 17 to 23 corresponded to the branched polymer and the area under the curve from counts 23 to 26 corresponded to the linear polymer. The latter portion decreased relative to the former at higher temperature. At higher concentration the monomer led to crosslinked polymer. The elemental analysis would not change depending on the degree of branching or crosslinking.

Poly(2-methoxyallyl 2'-carboethoxyallyl ether)

The polymer formed was soluble in benzene, chloroform, acetone DMF and DMSO. Characterization was done using IR, NMR (C 13 and proton), elemental analysis and GPC. The GPC curves again showed a bimodal distribution indicating a mixture of branched and linear polymer. The NMR data, hence, were not interpreted.

Conclusion on Polymerization of Monomers

For polymers of 2-carboethoxyallyl 2'-methoxyallyl ether and 2-cyanoallyl 2'-phenylallyl ether, no definite conclusions could be drawn regarding "charge transfer." At lower temperatures a complex could be formed. However, at higher temperatures as the complex tends to break up, reactivity ratios would tend to play a dominant part. However this does not rule out, at lower temperatures, kinetic

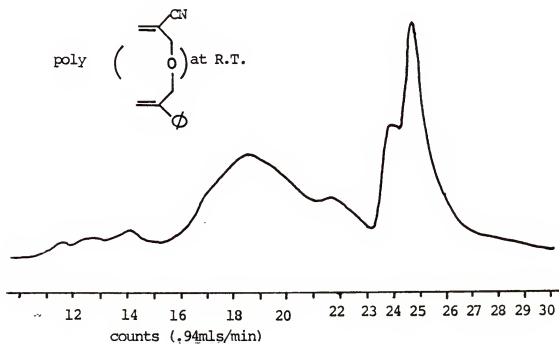
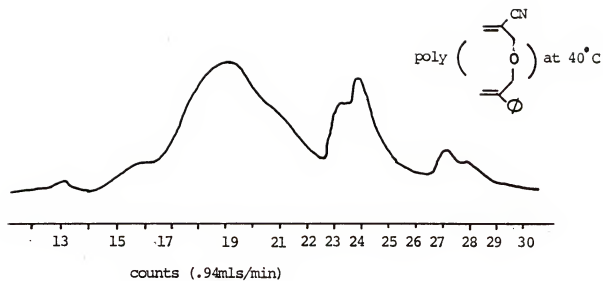
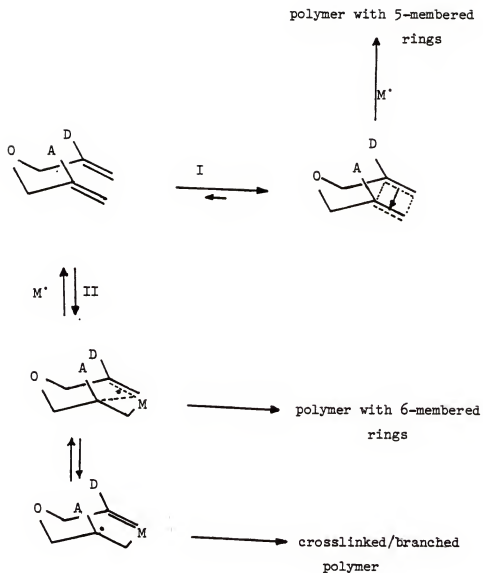


Fig. 24: GPC curves for polymers (in DMF) formed at R.T. and 40°C

control of ring formation and intermolecular propagation leading to a linear cyclopolymer with five-membered rings as per the mechanism of Butler² or six-membered rings as per the mechanism of Butler and Matsumoto⁶⁶ and Butler et al.⁶⁷ Unsaturation remaining in the polymers corresponding to the α -methoxyvinyl ether and styryl moieties leads one to conclude that these two moieties could perhaps lead to crosslinking or branching due to the relative stability of their radicals at higher temperatures. The facile homopolymerization of α -methyl acrylonitrile and methyl methacrylate⁶⁸ would have to be taken into account. For 2-chloroallyl 2'-phenylallyl ether, one could perhaps assume that no "charge transfer" is taking place between the 2 unsaturation units. The α -methylvinyl chloride moiety does not polymerize in a cyclo-fashion as can be seen from the attempted polymerization of 2-chloroallyl ether.

From the polymers of 2-carboethoxyallyl 2'-phenylallyl ether Scheme 8 is proposed. Initial attack of the initiator perhaps occurs at the point of unsaturation having the donor group. This would be the more reactive of the double bonds. The first equilibrium has been shown to exist but it may be largely lying to the right due to lack of observation of any other peaks in the NMR spectra. At 60° C, however, the stability of the benzyl radical and the methoxyvinyl radical may be a factor since equilibrium II (Scheme 8) would play an important role due to the break up of the "charge transfer" complex²⁶ and the consequent lower contribution of the other pathway. Thus



Scheme 8: Possible paths for polymerizations of monomers.

with a highly reactive acceptor substituted vinyl radical (relative to donor substituted vinyl radical) intermolecular reaction could occur over ring closure as is indicated by the polymerization rates. Thus the proportion of branched polymer increases at higher temperatures in the case of poly(2-cyanoallyl 2-phenyallyl ether) and poly(2-methoxyallyl 2'-carboethoxyallyl ether). This would leave the substituted benzyl and the substituted α -methoxyvinyl unsaturation which is seen in the case of the branched polymers in both the carbon and proton NMR spectra.

Frontier Molecular Orbital Analysis

For the monomers studied, an analysis would involve considering each molecule as two separate entities. The entities would be substituted vinyl groups, the substituents being electron withdrawing (A) and electron donating (D) or conjugating (C). The related energy levels of frontier orbitals of ethylene and some monosubstituted ethylenes are shown in Figure 25 for comparison. Here the size of the circle is roughly in proportion to the coefficient on the vinyl carbon in the frontier orbital; the shaded and unshaded ones are of opposite signs of the coefficient in the molecular orbital representation.

"Charge transfer" complexes are predicted to have favored interactions. Maximum overlap between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular

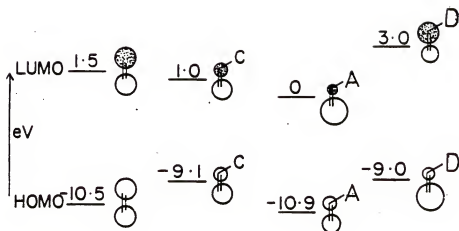
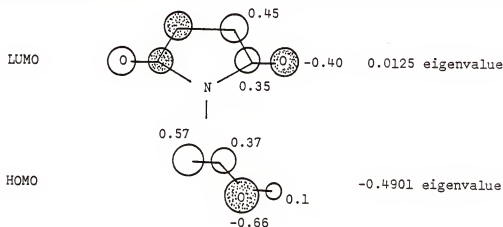


Fig. 25: Frontier orbital energies and coefficients of ethylene and monosubstituted ethylenes.

orbital (LUMO) of the acceptor would lead to the maximum amount of charge-transfer stabilization.

In the system studied subsequently, the LUMO of the acceptor, N-methylmaleimide, and the HOMO of the donor, methyl vinyl ether, are represented below with the area of the circle being proportional to



the coefficient of the p_2 orbital, the atomic orbital of the atom mainly contributing to the molecular orbital. Maximum overlap could therefore be obtained with the stereochemistry of the complex as proposed by Butler and Olson.²⁵ This is indeed seen in the next chapter when a high energy of stabilization is obtained from calculations. Also polymers obtained from these monomers support this structure.

For the system studied, in order to determine "charge transfer" via frontier orbitals, the system could be looked at as shown in Figure 26. These combinations as can be seen from Figure 25 would be the combinations that would give the minimum energy difference and the maximum overlap. Thus "charge transfer" would be maximized. The energy levels and the coefficients would vary with substituent. This

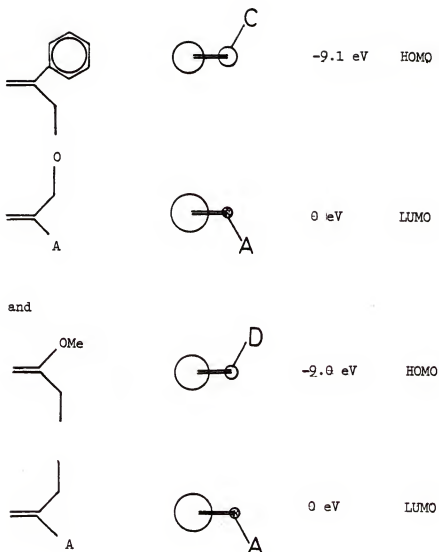
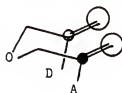


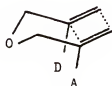
Fig. 26: Representations of the systems studied.

interaction is seen experimentally as discussed under Section D of this chapter.

Thus one could expect a structure such as

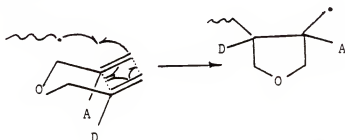


and the expected geometry may be visualized as



With no interaction existing, the singly occupied molecular orbital (SOMO) of the vinyl group with the acceptor substituent interacting with the HOMO of the other vinyl species (having the C or D substituent) would lead to a six-membered radical. The vinyl group having the acceptor substituent would have to be the one forming the radical species initially since it has a relatively low energy SOMO.²⁷ This would be more sensitive to the polarization of the HOMO of the other vinyl group which is raised in energy due to the C or D substituent leading to a six-membered ring. This is indeed what is observed at higher temperatures in the absence of "charge transfer" complexation.

However, in the presence of complexation, a concerted addition of the complex to the chain end would lead to five-membered ring formation thus:

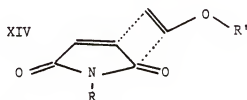


The next complex could add to the radical end. This would explain the five-membered ring predominance at 40° C and the six-membered ring proportion increasing upon polymerization at 60° C.

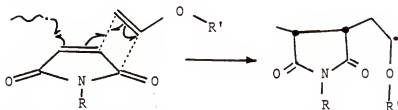
CHAPTER 4 THEORETICAL CALCULATIONS

Introduction

Butler and Olson²⁵ have, on the basis of stereochemistry observed, cited the complex (XIV) in the copolymerization of N-substituted maleimides and vinyl ethers.



The stereochemical results were rationalized by invoking the attack of the radical chain end on the side of the complex that is syn to the vinyl ether as shown:



The mechanism cited was thus a concerted addition of the complex to the chain end. The next complex could add to either side of the vinyl ether radical, thus explaining the random selective stereochemistry between the vinyl ether methine carbon and the methines of adjacent succinimide units observed in the copolymers.

It was intended that theoretical molecular-orbital calculations be carried out on complex XIV.

The intermolecular interaction in charge-transfer complexes (a form of molecular association) has been treated most frequently by means of perturbation theory.⁵⁴ However a molecular orbital treatment considering the complex as a single molecule seemed to be more suitable for giving quantitative predictions. As yet, the results of some molecular-orbital (MO) calculations using several semi-empirical all valence electron methods have not been very successful. Extended Huckel Theory (EHT) calculations on some calculations of this type failed to find any stable arrangement.⁵⁵

Complete Neglect of Differential Overlap/2 (CNDO/2)⁵⁹ calculations on the Tetracyanoethylene (TCNE)-benzene complex are reported.⁵⁶ The CNDO/2 method overestimates the stabilization energy considerably and the minima are at too short distances of the complex components. The basic purpose behind such a calculation, however, is the elucidation of those factors which dictate the observed relative intermolecular geometric characteristic of the majority of both charge-transfer and charge-resonance complexes.

The PCILO^{60,61} (perturbative configuration interaction using localized orbitals) method in the field of charge-transfer interaction has been applied to calculate intermolecular energies in the cis-2-bulene-lithium (I)⁵⁷ complex and complexes of thiazoles with tetracyanoethylene⁵⁸ (TCNE). Again in these cases, the too short distances of the complex components and the slight overestimation of the stabilization energy given by the PCILO method

may be caused by using the CNDO parameterization. This effect is intensified by the so-called "basis-extension" effect.^{58,62} The program PCILO calculates the electronic ground state energy and the one particle density matrix. Essentially it looks at the molecule as an assembly of two center, two electron molecules (chemical bonds) in interaction, the interaction being treated by perturbation theory in an antisymmetrized basis. The method relies on four fundamental steps:

- (1) Building up the bonding and antibonding orbitals.
- (2) The antibonding orbitals are used for the construction of Slater determinants' corresponding to excited configurations.
- (3) The bonding orbitals are used to construct a Slater determinant which is the zero-th order wave function for the molecule.
- (4) In the basis of all these determinants the molecular Hamiltonian is represented by a configuration interaction matrix. The eigen-value and eigen vector are calculated by a Rayleigh-Schrodinger perturbation series.

The program in its present form applies the zero differential overlap (ZDO) simplification in order to force the starting set of bonding orbitals to be orthogonal. The application of CNDO/2 approximations for the molecular integrals further simplifies the calculations.

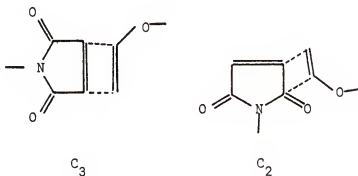
Table 22: Comparison of CNDO and PCIO determinations with experimental data, ΔE -kcal/mole, R-A°.

Charge-Transfer Complex	PCIO		CNDO/2		Experimental	
	$-\Delta E$	R	$-\Delta E$	R	$-\Delta E$	R
benzene- tetracyanoethylene (TCNE)						
Configuration 1	22.5	2.20	125	1.75	3.35 2.54	3.2-3.5
Configuration 2	23.3	2.20	143	1.75		
direne-TCNE						
Configuration 1	5.7	2.50	-	-	5.5 5.32	3.2-3.5
Configuration 2	3.5	2.75	-	-		
hydrofuranone- quinone	5.6	2.60	-	-	2.9 2.4 5.2	3.33
	2.4	2.60				
ethylene-fluorine	27.7	1.60	37	1.46	-	-
ethylene-chlorine	8.7	2.25	62	2.26	2-3	3.0

Calculation Details

The ZINDO program, a geometry optimization analytical gradient INDO program,⁶³ was used to initially optimize the geometrics of N-methylmaleimide and methyl vinyl ether. The input was done via the Quantum Chemistry Interactive Program Utility (QUIPU).⁶⁴ After a ball and stick geometry optimizer on the initial geometry sketched in, it took 46 cycles of ZINDO for the N-methylmaleimide and 106-cycles for the methyl vinyl ether for the optimization to take place. The final optimized geometry of N-methylmaleimide and methyl vinyl ether are listed in Tables 23 and 24 respectively and the z-axis views are shown in Figure 27 corresponding to the tables.

Similarly structures C₂ and C₃



were optimized using ZINDO utilizing 158 and 170 cycles of ZINDO respectively. The geometries likewise are listed in Tables 26 and 27 and the z-axis views in Figure 28 corresponding to the tables. For each of the structures obtained a CNDO/2 calculation was also done. The final analytical gradients for each of the four structures is shown in Tables 28-31. The CNDO/2 density matrices and the gross charge density are listed in the Appendix.

Table 23: Parameters of methyl vinyl ether.

	#	X	Y	Z
H	1	-2.155475	-1.118756	-0.011722
H	2	-0.231796	1.350768	-0.021649
C	3	-1.837222	-0.074178	-0.022282
C	4	-0.564335	0.303948	-0.013968
H	5	1.709325	0.889606	-0.650592
H	6	-2.660554	0.641938	-0.042616
O	7	0.445465	-0.625126	-0.005711
C	8	1.685946	-0.016889	-0.025861
H	9	2.006073	0.246262	0.995184
H	10	2.406381	-0.741222	-0.440396

bond distance (Angstroms)		atom #
C -H	1.092035	(3- 1)
C -H	1.098396	(4- 2)
C -C	1.327889	(4- 3)
H -C	1.091380	(6- 3)
O -C	1.372204	(7- 4)
C -H	1.101167	(8- 5)
C -O	1.381721	(8- 7)
H -C	1.101936	(9- 8)
H -C	1.102508	(10- 8)

bond angles				atom #
ANGLE	H	-C	-H	(1- 3- 6)
ANGLE	H	-C	-C	(1- 3- 4)
ANGLE	H	-C	-C	(6- 3- 4)
ANGLE	O	-C	-H	(7- 4- 2)
ANGLE	O	-C	-C	(7- 4- 3)
ANGLE	H	-C	-C	(2- 4- 3)
ANGLE	C	-O	-C	(4- 7- 8)
ANGLE	H	-C	-H	(10- 8- 5)
ANGLE	H	-C	-O	(10- 8- 7)
ANGLE	H	-C	-H	(10- 8- 9)
ANGLE	H	-C	-O	(5- 8- 7)
ANGLE	H	-C	-H	(5- 8- 9)
ANGLE	O	-C	-H	(7- 8- 9)

Table 24: Parameters of N-methylmaleimide.

	#	X	Y	Z
H	1	2.468957	-1.316618	0.026650
H	2	2.422603	1.401612	0.024827
C	3	1.607880	-0.644828	0.016713
C	4	1.585969	0.699810	0.015605
O	5	-0.209097	-2.320781	-0.006374
C	6	0.225542	-1.119139	0.005417
N	7	-0.632975	-0.011410	0.012919
C	8	0.188179	1.124291	0.002032
O	9	-0.292639	2.308335	-0.014892
C	10	-2.049829	-0.010518	0.015301
H	11	-2.429451	0.911421	0.480609
H	12	-2.441137	-0.870347	0.579238
H	13	-2.456109	-0.064028	-1.007527

bond distance (Angstroms)		atom #
C	-H	(3- 1)
C	-H	(4- 2)
C	-C	(4- 3)
C	-C	(6- 3)
C	-O	(6- 5)
N	-C	(7- 6)
C	-C	(8- 4)
C	-N	(8- 7)
O	-C	(9- 8)
C	-N	(10- 7)
H	-C	(11-10)
H	-C	(12-10)
H	-C	(13-10)

bond angles				atom #
ANGLE	H	-C	-C	(1- 3- 6)
ANGLE	H	-C	-C	(1- 3- 4)
ANGLE	C	-C	-C	(6- 3- 4)
ANGLE	C	-C	-H	(8- 4- 2)
ANGLE	C	-C	-C	(8- 4- 3)
ANGLE	H	-C	-C	(2- 4- 3)
ANGLE	C	-C	-O	(3- 6- 5)
ANGLE	C	-C	-N	(3- 6- 7)
ANGLE	O	-C	-N	(5- 6- 7)
ANGLE	C	-N	-C	(10- 7- 6)
ANGLE	C	-N	-C	(10- 7- 8)
ANGLE	C	-N	-C	(6- 7- 8)
ANGLE	C	-C	-N	(4- 8- 7)
ANGLE	C	-C	-O	(4- 8- 9)
ANGLE	N	-C	-O	(7- 8- 9)
ANGLE	H	-C	-N	(13-10- 7)
ANGLE	H	-C	-H	(13-10-12)
ANGLE	H	-C	-H	(13-10-11)
ANGLE	N	-C	-H	(7-10-12)
ANGLE	N	-C	-H	(7-10-11)
ANGLE	H	-C	-H	(12-10-11)

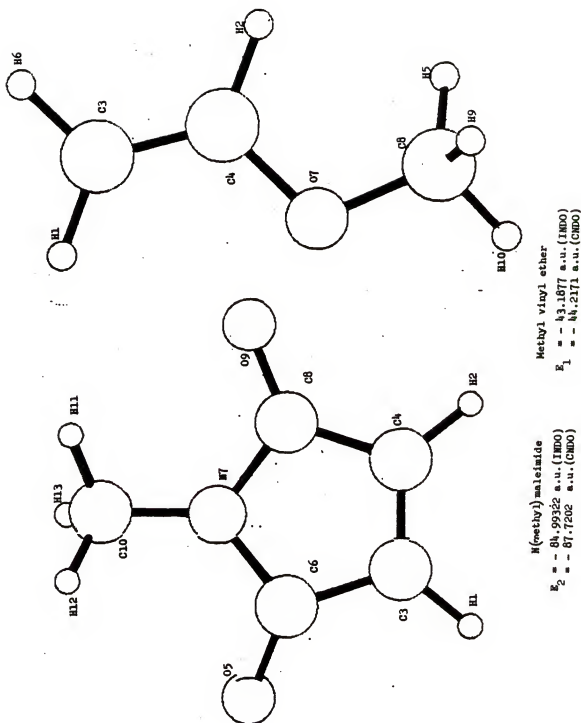


Fig. 27: Z-axis view of ZINDO geometry optimized molecules

Table 25: Coordinates of C_2 and C_3 .

C_2				
	#	X	Y	Z
H	1	-0.047261	-0.173410	2.052074
H	2	-0.155125	-1.668463	1.095092
H	3	-1.232495	1.749109	-0.552373
H	4	2.184063	-2.056608	1.116932
C	5	0.390623	-0.718163	1.202615
H	6	-0.670409	-0.700898	-0.625612
C	7	-0.272027	1.401415	-0.173834
C	8	1.867711	-1.036828	1.378780
C	9	0.075794	-0.010309	-0.192795
O	10	0.994258	3.482943	0.381848
C	11	0.777943	2.210983	0.205857
C	12	1.616201	-0.002367	0.367804
O	13	1.279182	-0.285027	-0.957784
O	14	2.467187	-0.511035	2.515959
N	15	1.844923	1.355599	0.658698
C	16	2.996969	-1.546737	3.264033
H	17	2.287192	-2.379177	3.385536
H	18	3.121724	2.421299	1.901999
C	19	2.150495	1.782710	1.005145
H	20	3.814882	0.929178	1.212002
H	21	3.925987	-1.922564	2.808128
H	22	3.232079	-1.134969	4.258494
H	23	3.598419	2.368683	0.186215
C_3				
	#	X	Y	Z
H	1	-1.386499	5.210777	-0.833059
H	2	-5.968158	4.880950	-0.881623
H	3	-3.822517	4.492895	1.324146
O	4	-3.394825	5.110639	-0.589539
C	5	-2.150468	5.398664	-0.061567
H	6	-2.111048	6.464612	0.215709
H	7	-6.172678	5.173616	0.832432
C	8	-5.654066	4.501787	0.129825
C	9	-4.160453	4.338033	0.281423
H	10	-1.905240	4.796018	0.826672
H	11	-5.765467	2.879046	1.509824
C	12	-5.744148	3.032752	0.411025
C	13	-4.327551	2.894143	-0.110248
H	14	-4.333150	2.847267	-1.218958
O	15	-7.459940	1.469682	-0.575175
C	16	-6.316233	1.781691	-0.101071
C	17	-4.054110	1.501000	0.261834
O	18	-3.019094	0.884686	0.684292
N	19	-5.277694	0.841652	0.034649
H	20	-6.522173	-0.807283	-0.140700
C	21	-5.455671	-0.564204	-0.023341
H	22	-4.908936	-1.002344	-0.873406
H	23	-5.089802	-1.045983	0.896849

Table 26: Bond angles and bond distances (Å) of C₂.

bond angles				atom #	
ANGLE	H	-C	-H	107.788	(2- 5- 1)
ANGLE	H	-C	-C	108.165	(2- 5- 8)
ANGLE	H	-C	-C	101.515	(2- 5- 9)
ANGLE	H	-C	-C	113.628	(1- 5- 8)
ANGLE	H	-C	-C	112.147	(1- 5- 9)
ANGLE	C	-C	-C	112.685	(8- 5- 9)
ANGLE	H	-C	-C	125.828	(3- 7-11)
ANGLE	H	-C	-C	121.081	(3- 7- 9)
ANGLE	C	-C	-C	112.839	(11- 7- 9)
ANGLE	C	-C	-C	113.183	(12- 8- 5)
ANGLE	C	-C	-H	122.608	(12- 8- 4)
ANGLE	C	-C	-O	111.778	(12- 8-14)
ANGLE	C	-C	-H	116.495	(5- 8- 4)
ANGLE	C	-C	-O	115.759	(5- 8-14)
ANGLE	H	-C	-O	114.960	(4- 8-14)
ANGLE	H	-C	-C	101.448	(6- 9- 5)
ANGLE	H	-C	-C	116.765	(6- 9- 7)
ANGLE	H	-C	-C	140.492	(6- 9-12)
ANGLE	C	-C	-C	117.799	(5- 9- 7)
ANGLE	C	-C	-C	118.830	(5- 9-12)
ANGLE	C	-C	-C	102.452	(7- 9-12)
ANGLE	N	-C	-C	107.609	(15-11- 7)
ANGLE	N	-C	-O	115.742	(15-11-10)
ANGLE	C	-C	-O	136.632	(7-11-10)
ANGLE	C	-C	-N	120.641	(8-12-15)
ANGLE	C	-C	-O	123.525	(8-12-13)
ANGLE	C	-C	-C	113.145	(8-12- 9)
ANGLE	N	-C	-O	115.508	(15-12-13)
ANGLE	N	-C	-C	103.183	(15-12- 9)
ANGLE	O	-C	-C	123.526	(13-12- 9)
ANGLE	C	-O	-C	108.947	(16-14- 8)
ANGLE	C	-N	-C	119.418	(19-15-12)
ANGLE	C	-N	-C	125.326	(19-15-11)
ANGLE	C	-N	-C	113.438	(12-15-11)
ANGLE	H	-C	-H	108.741	(21-16-22)
ANGLE	H	-C	-O	110.785	(21-16-14)
ANGLE	H	-C	-H	109.370	(21-16-17)
ANGLE	H	-C	-O	106.863	(22-16-14)
ANGLE	H	-C	-H	108.701	(22-16-17)
ANGLE	O	-C	-H	112.274	(14-16-17)
ANGLE	H	-C	-N	110.679	(23-19-15)
ANGLE	H	-C	-H	107.904	(23-19-18)
ANGLE	H	-C	-H	107.846	(23-19-20)
ANGLE	N	-C	-H	110.480	(15-19-18)
ANGLE	N	-C	-H	111.608	(15-19-20)
ANGLE	H	-C	-H	108.192	(18-19-20)

Table 26-continued.

bond distance (Angstroms)		atom #
C -H	1.101123	(5- 2)
C -H	1.100036	(5- 1)
C -H	1.089349	(7- 3)
C -C	1.521305	(8- 5)
C -H	1.099361	(8- 4)
C -H	1.105017	(9- 6)
C -C	1.596040	(9- 5)
C -C	1.454064	(9- 7)
C -C	1.392192	(11- 7)
C -O	1.296855	(11-10)
C -C	1.458142	(12- 8)
C -C	1.639265	(12- 9)
O -C	1.396661	(13-12)
O -C	1.388887	(14- 8)
N -C	1.407482	(15-12)
N -C	1.427047	(15-11)
C -O	1.383099	(16-14)
H -C	1.100683	(17-16)
C -N	1.416675	(19-15)
C -H	1.101350	(19-18)
H -C	1.101234	(20-19)
H -C	1.100986	(21-16)
H -C	1.101718	(22-16)
H -C	1.102110	(23-19)

Table 27: Bond angles and bond distances of C₃.

bond angles			atom #
ANGLE	C	-O -C	111.809 (5- 4- 9)
ANGLE	H	-C -H	108.487 (10- 5- 1)
ANGLE	H	-C -O	113.244 (10- 5- 4)
ANGLE	H	-C -H	108.569 (10- 5- 6)
ANGLE	H	-C -O	108.738 (1- 5- 4)
ANGLE	H	-C -H	108.437 (1- 5- 6)
ANGLE	O	-C -H	109.261 (4- 5- 6)
ANGLE	C	-C -H	114.950 (12- 8- 2)
ANGLE	C	-C -H	116.733 (12- 8- 7)
ANGLE	C	-C -C	93.767 (12- 8- 9)
ANGLE	H	-C -H	106.617 (2- 8- 7)
ANGLE	H	-C -C	113.829 (2- 8- 9)
ANGLE	H	-C -C	117.881 (7- 8- 9)
ANGLE	H	-C -C	112.419 (3- 9- 8)
ANGLE	H	-C -C	114.401 (3- 9-13)
ANGLE	H	-C -O	110.082 (3- 9- 4)
ANGLE	C	-C -C	91.824 (8- 9-13)
ANGLE	C	-C -O	114.872 (8- 9- 4)
ANGLE	C	-C -O	115.476 (13- 9- 4)
ANGLE	C	-C -H	108.831 (8-12-11)
ANGLE	C	-C -C	142.517 (8-12-16)
ANGLE	C	-C -C	91.780 (8-12-13)
ANGLE	H	-C -C	102.703 (11-12-16)
ANGLE	H	-C -C	110.231 (11-12-13)
ANGLE	C	-C -C	99.574 (16-12-13)
ANGLE	C	-C -C	100.005 (17-13-12)
ANGLE	C	-C -H	102.365 (17-13-14)
ANGLE	C	-C -C	145.470 (17-13- 9)
ANGLE	C	-C -H	110.043 (12-13-14)
ANGLE	C	-C -C	94.215 (12-13- 9)
ANGLE	H	-C -C	107.519 (14-13- 9)
ANGLE	C	-C -O	133.392 (12-16-15)
ANGLE	C	-C -N	104.362 (12-16-19)
ANGLE	O	-C -N	122.245 (15-16-19)
ANGLE	C	-C -O	133.887 (13-17-18)
ANGLE	C	-C -N	103.983 (13-17-19)
ANGLE	O	-C -N	122.125 (18-17-19)
ANGLE	C	-N -C	124.441 (21-19-16)
ANGLE	C	-N -C	125.429 (21-19-17)
ANGLE	C	-N -C	110.118 (16-19-17)
ANGLE	H	-C -N	110.965 (23-21-19)
ANGLE	H	-C -H	108.334 (23-21-20)
ANGLE	H	-C -H	107.813 (23-21-22)
ANGLE	N	-C -H	110.184 (19-21-20)
ANGLE	N	-C -H	111.317 (19-21-22)
ANGLE	H	-C -H	108.116 (20-21-22)

Table 27-continued.

bond distance (Angstroms)		atom #
C -H	1.101885	(5- 1)
C -O	1.382077	(5- 4)
H -C	1.102126	(6- 5)
C -H	1.100536	(8- 2)
C -H	1.101802	(8- 7)
C -H	1.107030	(9- 3)
C -C	1.510102	(9- 8)
C -O	1.393492	(9- 4)
H -C	1.101039	(10- 5)
C -C	1.498417	(12- 8)
C -H	1.109702	(12-11)
C -C	1.515812	(13-12)
C -C	1.505363	(13- 9)
H -C	1.109715	(14-13)
C -C	1.467882	(16-12)
C -O	1.276813	(16-15)
C -C	1.467672	(17-12)
O -C	1.276547	(18-17)
N -C	1.407358	(19-16)
N -C	1.408372	(18-17)
C -N	1.418263	(21-19)
C -H	1.100131	(21-20)
H -C	1.101588	(22-21)
H -C	1.101236	(23-21)

Table 28: Energy gradient values of last cycle and summary of geometry optimization of cycles 95-106 for methyl vinyl ether.

Energy = -43.187676

Geometry 9		Atom:Energy Gradient (A.U.)		
		X	Y	Z
1		0.000278	-0.000202	0.000308
2		-0.000347	0.000150	-0.000405
3		-0.000528	-0.000195	-0.000057
4		-0.000160	0.000598	-0.000042
5		0.000066	0.000220	0.000546
6		-0.000297	-0.000184	-0.000551
7		0.000128	0.000634	0.000734
8		0.000394	-0.000059	0.000110
9		0.000743	-0.000637	0.000170
10		-0.000277	-0.000326	0.000813

Optimization Summary for Number 9 - Geometry
All Gradients Lt 0.00100 - Geometry Converged - Hurray

Summary of Geometry Optimization

Cycle	Opt Type	Energy	Convergence	Rms Grad
0	1	-43.187571	0.000000	0.000647
1	1	-43.187574	0.000000	0.000534
2	-1	-43.187578	0.000000	0.000524
3	1	-43.187581	0.000000	0.000464
4	1	-43.187583	0.000000	0.000631
5	1	-43.187620	0.000002	0.003397
6	-1	-43.187639	0.000001	0.002533
7	1	-43.187655	0.000000	0.001952
8	-1	-43.187674	0.000001	0.000455
9	1	-43.187676	0.000000	0.000407

Table 29: Energy gradient values of last cycle and summary of geometry optimization of cycles 38-46 for N-methylmaleimide.

Energy = -84.993218

Geometry 8

Atom:Energy Gradient (A.U.)

	X	Y	Z
1	-0.000471	0.000608	0.000130
2	-0.000523	-0.000326	0.000183
3	0.000059	-0.000553	0.000034
4	-0.000423	0.000438	0.000050
5	0.000885	0.000037	-0.000009
6	0.000704	-0.000009	-0.000120
7	-0.000320	-0.000157	-0.000458
8	0.000444	-0.000123	-0.000123
9	0.000475	-0.000739	-0.000029
10	-0.000382	0.000629	0.000243
11	0.000404	-0.000651	-0.000337
12	-0.000370	0.000584	-0.000086
13	-0.000482	0.000262	0.000522

Optimization Summary for Number 8 - Geometry

All Gradients Lt 0.00100 - Geometry Converged - Hurray

Summary of Geometry Optimization

Cycle	Opt Type	Energy	Convergence	Rms Grad
0	1	-84.992995	0.000002	0.001404
1	1	-84.993015	0.000004	0.001140
2	1	-84.993036	0.000001	0.000949
3	1	-84.993106	0.000012	0.004004
4	-1	-84.993184	0.000001	0.000919
5	1	-84.993194	0.000001	0.000680
6	1	-84.993202	0.000000	0.000503
7	1	-84.993211	0.000003	0.001092
8	1	-84.993218	0.000000	0.000414

Table 30: Energy gradient values of last cycle and summary of geometry optimization of cycles 155-158 for C₂.

Energy = -128.683929

Geometry 2		Atom:Energy Gradient (A.U.)		
		X	Y	Z
1		-0.000163	-0.000748	0.000142
2		-0.000680	-0.000241	-0.000154
3		0.000683	0.000471	-0.000026
4		-0.000316	-0.000689	0.000135
5		-0.000195	-0.000470	-0.000105
6		0.000179	0.000761	-0.000786
7		0.000133	0.000149	0.000479
8		-0.000310	-0.000575	-0.000033
9		0.000121	0.000207	0.000041
10		0.000922	-0.000324	0.000459
11		0.000533	0.000573	0.000613
12		0.000025	-0.000463	0.000244
13		0.000132	0.000014	0.000011
14		-0.000013	-0.000178	-0.000360
15		-0.000177	-0.000487	0.000479
16		0.000229	0.000280	0.000130
17		0.000538	0.000012	-0.000126
18		-0.000631	0.000052	-0.000342
19		-0.000204	-0.000011	-0.000274
20		0.000039	0.000133	-0.000561
21		0.000603	0.000639	0.000625
22		-0.000449	0.000762	0.000076
23		-0.000998	0.000132	-0.000616

Optimization Summary for Number 2 - Geometry

All Gradients Lt 0.00100 - Geometry Converged - Hurray

Summary of Geometry Optimization

Cycle	Opt Type	Energy	Convergence	Rms Grad
0	1	-128.683915	0.000004	0.000457
1	-1	-128.683923	0.000001	0.000433
2	1	-128.683929	0.000000	0.000427

Table 31: Energy gradient values of last cycle and summary of geometry optimization of cycles 167-170 for C₃.

Energy = -128.645698

Geometry 3		Atom:Energy Gradient (A.U.)		
		X	Y	Z
1		0.000120	-0.000153	0.000238
2		-0.000211	-0.000160	-0.000006
3		0.000778	0.000266	-0.000302
4		0.000075	-0.000196	-0.000158
5		-0.000072	0.000232	-0.000022
6		0.000077	0.000379	-0.000535
7		0.000071	-0.000167	0.000391
8		-0.000033	0.000040	0.000063
9		-0.000017	-0.000059	-0.000041
10		-0.000983	0.000623	0.000497
11		0.000459	-0.000204	0.000090
12		0.000105	0.000079	0.000112
13		0.000008	0.000105	0.000004
14		0.000007	0.000050	-0.000011
15		0.000381	0.000020	-0.000049
16		0.000117	-0.000054	-0.000379
17		0.000328	-0.000321	0.000890
18		-0.000480	-0.000304	-0.000205
19		0.000142	-0.000027	-0.000424
20		-0.000264	0.000202	-0.000041
21		-0.000169	-0.000157	-0.000066
22		-0.000268	-0.000237	-0.000086
23		-0.000172	0.000042	0.000043

Optimization Summary for Number 3 - Geometry

All Gradients Lt 0.00100 - Geometry Converged - Hurray

Summary of Geometry Optimization

Cycle	Opt Type	Energy	Convergence	Rms Grad
0	1	-128.645688	0.000001	0.000352
1	-1	-128.645692	0.000000	0.000309
2	-1	-128.645695	0.000000	0.000297
3	1	-128.645698	0.000000	0.000290

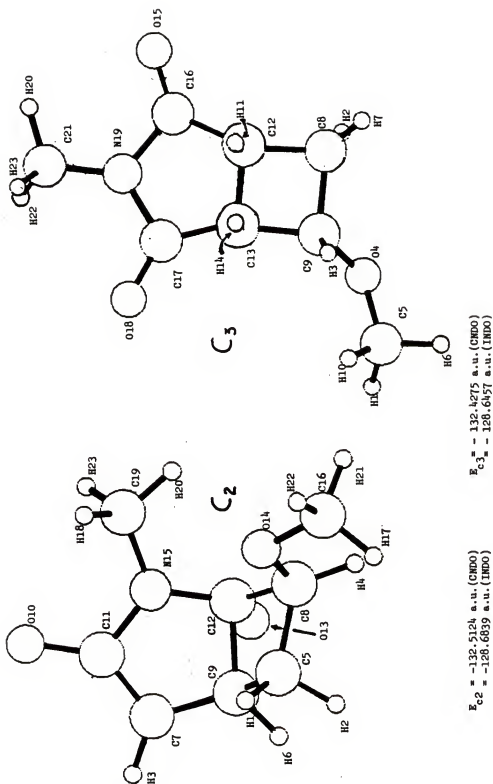


Fig. 28: Z-axis view of ZINDO geometry optimized molecules

CNDO/2 calculations treating the complex as a single moiety were also done at various distances between the components. Methyl vinyl ether (ZINDO optimized structure) in plane $z = \text{distance}$, was made to approach N-methylmaleimide (ZINDO optimized structure) in plane $z = 0$, along the z -axis, i.e., along parallel planes with bond 3-4 of methyl vinyl ether (Fig. 27) directly over bond 3-6 of N-methylmaleimide (Fig. 27). A view along this axis (2) is shown along with the potential diagram in Figure 29. The intermolecular interaction energy ΔE is obtained from the difference

$$\Delta E_{\text{compl}} = E_c(r) - E_c(\infty)$$

where $E_c(r)$ is the energy of the system with distance r between subsystems A and B and

$$E_c(\infty) = E_1 + E_2$$

The energy of stabilization ($-\Delta E_{\text{complex}}$) seemed to be maximum at an intermolecular distance of 1.75 Å. The energy of stabilization is calculated to be 75 kcal mole. The calculation done in the PCIOLO frame work⁶⁵ gave the energies depicted in Table 33. The energy of stabilization is again calculated from

$$\Delta E_{\text{compl}*} = E_c(r) - E_c(\infty)$$

$E_c(\infty)$ here is taken as $E_c(7.0)$. The sum of the energies of the separated molecules was not taken as the reference since in the program, lone pairs were to be replaced by fictitious atoms having a

Table 32: CNDO energy and difference in energy corresponding to various distances between molecules N-methylmaleimide and methyl vinyl ether.

d(Å)	-E (au)	-ΔE(au)	-ΔE(kcal/mole)
7.0	131.9373	1.87×10^{-5}	0.0117
6.0	131.9373	3.06×10^{-5}	0.0192
4.0	131.9374	1.383×10^{-4}	0.0868
3.5	131.9380	7.6×10^{-4}	0.4817
3.0	131.9418	4.544×10^{-3}	2.8516
2.5	131.9601	2.286×10^{-2}	14.3447
2.0	132.0218	8.46×10^{-2}	53.0649
1.75	132.0573	1.201×10^{-1}	75.3415
1.50	12.8622	-119.075	-74718.4
1.25	19.6092	-112.3281	-70484.77

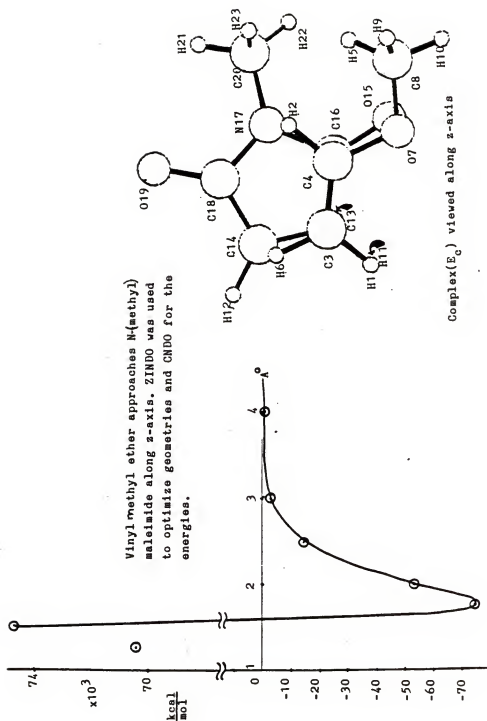


Fig. 29: Plot of $\Delta E_{\text{comp1}} = E_c - (E_1 + E_2)$ vs. distance.

zero nuclear charge and the number of lone pairs in the complex (9) are not the same as the sum of the lone pairs in the separated components (7).

A plot of the fourth order corrected energy versus distance is shown in Figure 30. The energy of stabilization was maximum at an intermolecular distance of 4.2 Å for the fourth order corrected plot. The energy of stabilization was calculated to be 395 kcal/mole.

The coordinates for the complex with the moieties at a distance of 7.0 Å are listed in Table 34.

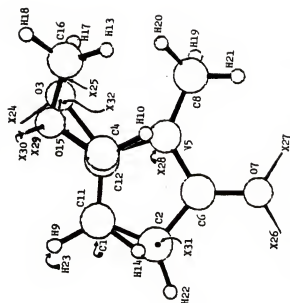
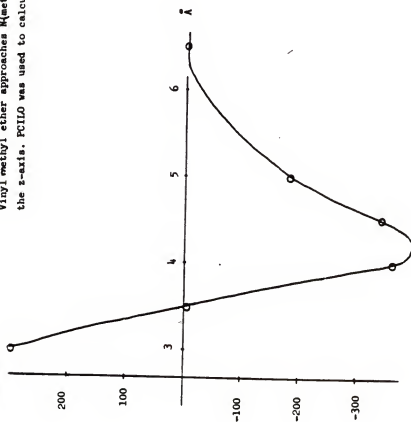
Before the energies were calculated, care was taken that the bond polarities were adjusted such that the polarization energy is minimized and hence converges. This is done in the supplied program by recalculation. The 'del' parameters in case the 'POL0' subroutine does not cause the polarization energy to converge within the twenty cycles, for which the program is adjusted.

Discussion

The ZINDO optimization of C_2 would give a higher energy of stabilization than is calculated by the CNDO method since this would involve minimization of the steric and other electronic factors (rehybridization, etc.) that effect the conformation corresponding to the minima in Figure 29. The ZINDO optimized structure would not be the same as the actual structure and hence the data would have to be judged qualitatively rather than quantitatively. As one can see from the formal charges of the carbons involved "charge transfer" has

kcal/mole

Vinyl methyl ether approaches M(methyl)maleimide along the z-axis. PCILLO was used to calculate the energies(fourth order).



Complex (F_C^*) viewed along the z-axis.

Fig. 30: Plot of $\Delta E_{\text{comp1}*} = E_{C^*}(r) - E_{C^*}(\infty)$ vs. distance.

Table 33: PCILO energy and difference in energy corresponding to various distances between molecules N-methylmaleimide and methyl vinyl ether.

distance	Order				total after 4th order	ΔE compl*
	zero + 1st	2nd corr	3rd corr	4th corr		
7.0	-81567.61	-856.855	-519.087	-425.392	-83368.94	0
6.5	-81567.73	-856.631	-518.600	-424.666	-83367.62	+1.319
5.0	-81457.03	-1208.349	-774.369	-111.611	-83551.36	-182.42
4.5	-81541.06	-1148.428	-728.849	-288.748	-83707.08	-338.14
4.0	-81536.49	-1132.748	-740.938	-321.718	-83731.88	-362.94
3.5	-81567.03	-972.601	-517.099	-316.887	-83373.62	-4.674
3.0	-81649.63	-813.138	-345.600	-262.518	-83070.89	+298.05
2.5	-81772.13	-691.085	-203.728	-175.179	-82842.12	+526.82
2.0	-82002.43	-606.165	-133.117	-114.558	-82856.27	+512.67
1.5	-81991.07	-636.631	-69.434	-133.997	-82831.13	+537.81
N-methyl maleimide	-54732.72	-381.715	-71.673	-47.561	-55233.16	
Methyl vinyl ether	-26155.52	-622.636	-46.575	-1204.213	-27935.80	

Table 34: Coordinates of the complex (E_{C^*}) with the moieties at a distance of 7.0 Å.

	#	X	Y	Z
C	1	0.000000	0.000000	0.000000
C	2	-0.415600	-1.278900	-0.011600
O	3	2.627000	0.995600	0.000000
C	4	1.461500	0.000000	0.000000
N	5	1.914000	-1.326400	0.003500
C	6	0.768800	-2.134000	-0.020800
O	7	0.839500	-3.409900	-0.044400
C	8	3.253800	-1.787200	0.013600
H	9	-0.602500	0.910800	7.000000
H	10	1.944700	-0.908800	6.887200
C	11	0.000000	0.000000	7.000000
C	12	1.327900	0.000000	7.000000
H	13	3.670200	0.075800	7.652500
H	14	-0.585400	-0.921100	7.002200
O	15	2.031400	1.178100	7.014700
C	16	3.393500	0.947900	7.039700
H	17	3.781700	0.802900	6.018700
H	18	3.875300	1.840700	7.471400
H	19	3.663300	-1.862600	-1.006600
H	20	3.898600	-1.104100	0.586400
H	21	3.310100	-2.785000	0.473700
H	22	-1.434800	-1.671200	-0.012400
H	23	-0.596500	0.914800	0.010500
X	24	1.901400	1.928100	0.000100
X	25	3.250700	0.842200	-0.000100
X	26	0.002500	-3.956900	-0.059400
X	27	1.731800	-3.861300	-0.047700
X	28	1.895400	-1.330100	1.003300
X	29	1.774300	1.700900	7.827400
X	30	1.804700	1.703200	6.194400
X	31	-0.415600	-1.278900	0.988400
X	32	2.262700	0.995600	1.000000

taken place. The PCILO program takes into account fourth order energy correction which is not the same as previously used^{57,58} (only went to third order). Again the data would have to be judged qualitatively. The distance of 4.2 Å seems to be large for charge-transfer complexes and the energy of stabilization also particularly large. Once again this would be an effect of numerous assumptions, approximations and estimations.

The fact one should consider here would be that the total energy of the complex is approximately the same as calculated by the CNDO/2 and the PCILO program (132.0573 au or 82864.64 kcal/mole via CNDO/2 and 83731 kcal/mole via PCILO).

However, one should remember that the PCILO method depends on the CNDO parameterization.

Conclusions

Qualitatively one can say:

- (a) One could have theoretically (PCILO and CNDO/2) predicted a "charge transfer" intermediate for the two reacting monomers.
- (b) Of the possible intermediates (C_2 and C_3) C_2 is more stable as predicted experimentally and hence is the intermediate.

APPENDIX

CNDO/2 DENSITY MATRICES AND GROSS CHARGE DENSITIES FOR
N-METHYLMALEIMIDE, METHYL VINYL ETHER, C₂ AND C₃, RESPECTIVELY

N-Methylmaleimide

1	1	M	5	1	0.9626	-0.0665	0.5475	0.6455	-0.4963	0.0059	-0.0047	0.0260	0.0345	10	-0.0504	-0.0142
2	2	M	5	2	-0.0665	0.9624	-0.0849	-0.0246	-0.0354	-0.0005	0.5460	0.6278	0.5180	0.0062	-0.0084	
3	3	UUUU	5	3	0.5475	-0.0849	1.0317	0.0411	-0.0458	0.0046	0.3444	0.2093	-0.0423	0.0078	-0.0025	
4	4	UUUU	5	4	0.6455	-0.0246	0.0411	0.9956	0.0398	0.0000	0.5577	0.0209	-0.0426	0.0078	-0.0025	
5	5	UUUU	5	5	-0.0665	0.9624	-0.0849	0.0394	1.0269	0.0005	0.5460	0.6278	0.5180	0.0062	-0.0084	
6	6	UUUU	5	6	0.5475	-0.0849	1.0317	0.0411	-0.0458	0.0046	0.3444	0.2093	-0.0423	0.0078	-0.0025	
7	7	UUUU	5	7	0.6455	-0.0246	0.0411	0.9956	0.0398	0.0000	0.5577	0.0209	-0.0426	0.0078	-0.0025	
8	8	UUUU	5	8	-0.0665	0.9624	-0.0849	0.0394	1.0269	0.0005	0.5460	0.6278	0.5180	0.0062	-0.0084	
9	9	UUUU	5	9	0.5475	-0.0849	1.0317	0.0411	-0.0458	0.0046	0.3444	0.2093	-0.0423	0.0078	-0.0025	
10	10	UUUU	5	10	0.6455	-0.0246	0.0411	0.9956	0.0398	0.0000	0.5577	0.0209	-0.0426	0.0078	-0.0025	
11	11	UUUU	5	11	-0.0665	0.9624	-0.0849	0.0394	1.0269	0.0005	0.5460	0.6278	0.5180	0.0062	-0.0084	
12	12	UUUU	5	12	0.5475	-0.0849	1.0317	0.0411	-0.0458	0.0046	0.3444	0.2093	-0.0423	0.0078	-0.0025	
13	13	UUUU	5	13	0.6455	-0.0246	0.0411	0.9956	0.0398	0.0000	0.5577	0.0209	-0.0426	0.0078	-0.0025	
14	14	UUUU	5	14	-0.0665	0.9624	-0.0849	0.0394	1.0269	0.0005	0.5460	0.6278	0.5180	0.0062	-0.0084	
15	15	UUUU	5	15	0.5475	-0.0849	1.0317	0.0411	-0.0458	0.0046	0.3444	0.2093	-0.0423	0.0078	-0.0025	
16	16	UUUU	5	16	0.6455	-0.0246	0.0411	0.9956	0.0398	0.0000	0.5577	0.0209	-0.0426	0.0078	-0.0025	
17	17	UUUU	5	17	-0.0665	0.9624	-0.0849	0.0394	1.0269	0.0005	0.5460	0.6278	0.5180	0.0062	-0.0084	
18	18	UUUU	5	18	0.5475	-0.0849	1.0317	0.0411	-0.0458	0.0046	0.3444	0.2093	-0.0423	0.0078	-0.0025	
19	19	UUUU	5	19	0.6455	-0.0246	0.0411	0.9956	0.0398	0.0000	0.5577	0.0209	-0.0426	0.0078	-0.0025	
20	20	UUUU	5	20	-0.0665	0.9624	-0.0849	0.0394	1.0269	0.0005	0.5460	0.6278	0.5180	0.0062	-0.0084	
21	21	UUUU	5	21	0.5475	-0.0849	1.0317	0.0411	-0.0458	0.0046	0.3444	0.2093	-0.0423	0.0078	-0.0025	
22	22	UUUU	5	22	0.6455	-0.0246	0.0411	0.9956	0.0398	0.0000	0.5577	0.0209	-0.0426	0.0078	-0.0025	
23	23	UUUU	5	23	-0.0665	0.9624	-0.0849	0.0394	1.0269	0.0005	0.5460	0.6278	0.5180	0.0062	-0.0084	
24	24	UUUU	5	24	0.5475	-0.0849	1.0317	0.0411	-0.0458	0.0046	0.3444	0.2093	-0.0423	0.0078	-0.0025	
25	25	UUUU	5	25	0.6455	-0.0246	0.0411	0.9956	0.0398	0.0000	0.5577	0.0209	-0.0426	0.0078	-0.0025	
26	26	UUUU	5	26	-0.0665	0.9624	-0.0849	0.0394	1.0269	0.0005	0.5460	0.6278	0.5180	0.0062	-0.0084	
27	27	UUUU	5	27	0.5475	-0.0849	1.0317	0.0411	-0.0458	0.0046	0.3444	0.2093	-0.0423	0.0078	-0.0025	
28	28	UUUU	5	28	0.6455	-0.0246	0.0411	0.9956	0.0398	0.0000	0.5577	0.0209	-0.0426	0.0078	-0.0025	
29	29	UUUU	5	29	-0.0665	0.9624	-0.0849	0.0394	1.0269	0.0005	0.5460	0.6278	0.5180	0.0062	-0.0084	
30	30	UUUU	5	30	0.5475	-0.0849	1.0317	0.0411	-0.0458	0.0046	0.3444	0.2093	-0.0423	0.0078	-0.0025	
31	31	UUUU	5	31	0.6455	-0.0246	0.0411	0.9956	0.0398	0.0000	0.5577	0.0209	-0.0426	0.0078	-0.0025	
32	32	UUUU	5	32	-0.0665	0.9624	-0.0849	0.0394	1.0269	0.0005	0.5460	0.6278	0.5180	0.0062	-0.0084	
33	33	UUUU	5	33	0.5475	-0.0849	1.0317	0.0411	-0.0458	0.0046	0.3444	0.2093	-0.0423	0.0078	-0.0025	
34	34	UUUU	5	34	0.6455	-0.0246	0.0411	0.9956	0.0398	0.0000	0.5577	0.0209	-0.0426	0.0078	-0.0025	
35	35	UUUU	5	35	-0.0665	0.9624	-0.0849	0.0394	1.0269	0.0005	0.5460	0.6278	0.5180	0.0062	-0.0084	
36	36	UUUU	5	36	0.5475	-0.0849	1.0317	0.0411	-0.0458	0.0046	0.3444	0.2093	-0.0423	0.0078	-0.0025	
37	37	UUUU	5	37	0.6455	-0.0246	0.0411	0.9956	0.0398	0.0000	0.5577	0.0209	-0.0426	0.0078	-0.0025	

				34	35	36	37
1	1	H	S	0.0003	0.0151	-0.0079	0.0022
2	2	H	S	0.0003	-0.0092	0.0146	0.0035
3	3	C	S	-0.0002	-0.0067	0.0018	-0.0026
4	3	C	PX	0.0000	0.0114	-0.0076	0.0020
5	3	C	PY	-0.0001	0.0093	-0.0067	-0.0003
6	3	C	PZ	-0.0003	0.0104	0.0118	-0.0029
7	4	C	S	-0.0002	0.0035	-0.0073	-0.0031
8	4	C	PX	0.0000	-0.0099	0.0120	0.0031
9	4	C	PY	0.0001	0.0095	-0.0084	-0.0006
10	4	C	PZ	-0.0000	0.0095	0.0125	-0.0026
11	5	O	S	-0.0026	0.0037	0.0023	0.0008
12	5	O	PX	0.0050	0.0096	-0.0149	0.0021
13	5	O	PY	-0.0028	-0.0060	0.0070	-0.0001
14	5	O	PZ	-0.0171	0.0198	0.0289	-0.0444
15	6	C	S	-0.0005	0.0511	-0.0254	0.0069
16	6	C	PX	0.0005	-0.0541	0.0249	-0.0073
17	6	C	PY	0.0011	0.0520	-0.0325	0.0062
18	6	C	PZ	-0.0040	-0.0229	-0.0232	0.0480
19	7	4	S	-0.0030	-0.0072	-0.0072	-0.0044
20	7	N	PX	0.0045	-0.0002	0.0021	0.0038
21	7	N	PY	0.0001	-0.0402	0.0377	0.0026
22	7	N	PZ	0.1944	-0.0548	-0.0662	0.1209
23	8	C	S	-0.0000	-0.0283	0.0492	0.0114
24	8	C	PX	0.0009	0.0256	-0.0499	-0.0117
25	8	C	PY	-0.0011	0.0382	-0.0518	-0.0112
26	8	C	PZ	-0.0025	-0.0185	-0.0274	0.0484
27	9	O	S	-0.0031	0.0031	0.0044	0.0011
28	9	O	PX	0.0059	-0.0189	0.0081	0.0031
29	9	O	PY	0.0034	-0.0077	0.0046	0.0006
30	9	O	PZ	-0.0161	0.0251	0.0229	-0.0431
31	10	C	S	0.0007	0.4982	0.4990	0.4996
32	10	C	PX	-0.0007	-0.2803	-0.2972	-0.2928
33	10	C	PY	0.0004	0.7209	-0.6750	-0.0426
34	10	C	PZ	0.9835	0.3637	0.4401	-0.7970
35	11	H	S	0.3637	0.9972	-0.0257	-0.0363
36	12	H	S	0.4401	-0.0257	0.9995	-0.0361
37	13	H	S	-0.7970	-0.0363	-0.0361	1.0110

TOTAL ENERGY = -87.7201677308

BINDING ENERGY = -0.4607420139 A.U.

1	H	0.9626
2	C	0.9624
3	C	4.0246
4	C	4.0249
5	O	6.2996
6	C	3.6781
7	N	5.1707
8	C	3.6788
9	O	6.3004
10	C	3.8901
11	H	0.9972
12	H	0.9995
13	H	1.0110

DIPOLE MOMENTS

COMPONENTS	X	Y	Z
DENSITIES	1.39108	0.04018	0.10612
S ₀ P	0.76180	0.02339	-0.00364
P+D	0.00000	0.00008	0.00000
TOTAL	2.15378	0.06358	0.10248

DIPOLE MOMENT = 2.15715 DEBYES

Methyl vinyl Ether

1	1	1	5	0.9717	0.1456	2	0.5422	4	-0.7829	8	0.0046	0.0044	0.0252	0.0230	0.0006	11	0.0024
2	2	5	5	0.9156	0.0192	3	-0.0192	5	-0.0201	7	-0.0078	-0.0013	0.5493	0.2658	-0.7617	0.0007	0.0007
3	3	5	5	0.8427	0.0478	4	-0.0478	6	-0.0519	8	-0.0168	-0.0001	0.3904	-0.4773	-0.0025	9	0.0149
4	4	5	5	0.7693	0.0676	5	-0.0676	6	-0.0102	7	-0.0474	-0.0033	0.1150	-0.2080	-0.0075	10	0.0174
5	5	5	5	0.6966	0.0801	6	-0.0801	7	-0.0017	8	-0.0023	1.1004	0.0041	-0.6106	-0.0049	11	0.0118
6	6	5	5	0.6239	0.0904	7	-0.0904	8	0.5137	9	0.1540	0.0041	1.0276	-0.0472	0.0007	12	0.0357
7	7	5	5	0.5504	0.0983	8	-0.0983	9	-0.4866	10	-0.2980	-0.0106	-0.0541	0.3020	0.0004	13	0.0273
8	8	5	5	0.4776	0.1055	9	-0.1055	10	-0.1255	11	-0.0019	-0.0043	0.0007	0.0006	0.0006	14	0.0226
9	9	5	5	0.4049	0.1127	10	-0.1127	11	-0.0125	12	0.5019	0.0043	0.0007	0.0006	0.0006	15	0.0226
10	10	5	5	0.3322	0.1199	11	-0.1199	12	0.0174	13	0.0032	-0.0118	-0.0387	0.0273	0.0009	16	0.0226
11	11	5	5	0.2595	0.1271	12	-0.1271	13	0.0174	14	0.0032	-0.0118	-0.0387	0.0273	0.0009	17	0.0226
12	12	5	5	0.1868	0.1343	13	-0.1343	14	0.0174	15	0.0032	-0.0118	-0.0387	0.0273	0.0009	18	0.0226
13	13	5	5	0.1141	0.1415	14	-0.1415	15	0.0174	16	0.0032	-0.0118	-0.0387	0.0273	0.0009	19	0.0226
14	14	5	5	0.0414	0.1487	15	-0.1487	16	0.0174	17	0.0032	-0.0118	-0.0387	0.0273	0.0009	20	0.0226
15	15	5	5	0.0000	0.1559	16	-0.1559	17	0.0174	18	0.0032	-0.0118	-0.0387	0.0273	0.0009	21	0.0226
16	16	5	5	0.0000	0.1631	17	-0.1631	18	0.0174	19	0.0032	-0.0118	-0.0387	0.0273	0.0009	22	0.0226
17	17	5	5	0.0000	0.1703	18	-0.1703	19	0.0174	20	0.0032	-0.0118	-0.0387	0.0273	0.0009	23	0.0226
18	18	5	5	0.0000	0.1775	19	-0.1775	20	0.0174	21	0.0032	-0.0118	-0.0387	0.0273	0.0009	24	0.0226
19	19	5	5	0.0000	0.1847	20	-0.1847	21	0.0174	22	0.0032	-0.0118	-0.0387	0.0273	0.0009	25	0.0226
20	20	5	5	0.0000	0.1919	21	-0.1919	22	0.0174	23	0.0032	-0.0118	-0.0387	0.0273	0.0009	26	0.0226
21	21	5	5	0.0000	0.1991	22	-0.1991	23	0.0174	24	0.0032	-0.0118	-0.0387	0.0273	0.0009	27	0.0226
22	22	5	5	0.0000	0.2063	23	-0.2063	24	0.0174	25	0.0032	-0.0118	-0.0387	0.0273	0.0009	28	0.0226
23	23	5	5	0.0000	0.2135	24	-0.2135	25	0.0174	26	0.0032	-0.0118	-0.0387	0.0273	0.0009	29	0.0226
24	24	5	5	0.0000	0.2207	25	-0.2207	26	0.0174	27	0.0032	-0.0118	-0.0387	0.0273	0.0009	30	0.0226
25	25	5	5	0.0000	0.2279	26	-0.2279	27	0.0174	28	0.0032	-0.0118	-0.0387	0.0273	0.0009	31	0.0226
26	26	5	5	0.0000	0.2351	27	-0.2351	28	0.0174	29	0.0032	-0.0118	-0.0387	0.0273	0.0009	32	0.0226
27	27	5	5	0.0000	0.2423	28	-0.2423	29	0.0174	30	0.0032	-0.0118	-0.0387	0.0273	0.0009	33	0.0226
28	28	5	5	0.0000	0.2495	29	-0.2495	30	0.0174	31	0.0032	-0.0118	-0.0387	0.0273	0.0009	34	0.0226
29	29	5	5	0.0000	0.2567	30	-0.2567	31	0.0174	32	0.0032	-0.0118	-0.0387	0.0273	0.0009	35	0.0226
30	30	5	5	0.0000	0.2639	31	-0.2639	32	0.0174	33	0.0032	-0.0118	-0.0387	0.0273	0.0009	36	0.0226
31	31	5	5	0.0000	0.2711	32	-0.2711	33	0.0174	34	0.0032	-0.0118	-0.0387	0.0273	0.0009	37	0.0226
32	32	5	5	0.0000	0.2783	33	-0.2783	34	0.0174	35	0.0032	-0.0118	-0.0387	0.0273	0.0009	38	0.0226
33	33	5	5	0.0000	0.2855	34	-0.2855	35	0.0174	36	0.0032	-0.0118	-0.0387	0.0273	0.0009	39	0.0226
34	34	5	5	0.0000	0.2927	35	-0.2927	36	0.0174	37	0.0032	-0.0118	-0.0387	0.0273	0.0009	40	0.0226
35	35	5	5	0.0000	0.3000	36	-0.3000	37	0.0174	38	0.0032	-0.0118	-0.0387	0.0273	0.0009	41	0.0226
36	36	5	5	0.0000	0.3072	37	-0.3072	38	0.0174	39	0.0032	-0.0118	-0.0387	0.0273	0.0009	42	0.0226
37	37	5	5	0.0000	0.3144	38	-0.3144	39	0.0174	40	0.0032	-0.0118	-0.0387	0.0273	0.0009	43	0.0226
38	38	5	5	0.0000	0.3216	39	-0.3216	40	0.0174	41	0.0032	-0.0118	-0.0387	0.0273	0.0009	44	0.0226
39	39	5	5	0.0000	0.3288	40	-0.3288	41	0.0174	42	0.0032	-0.0118	-0.0387	0.0273	0.0009	45	0.0226
40	40	5	5	0.0000	0.3360	41	-0.3360	42	0.0174	43	0.0032	-0.0118	-0.0387	0.0273	0.0009	46	0.0226
41	41	5	5	0.0000	0.3432	42	-0.3432	43	0.0174	44	0.0032	-0.0118	-0.0387	0.0273	0.0009	47	0.0226
42	42	5	5	0.0000	0.3504	43	-0.3504	44	0.0174	45	0.0032	-0.0118	-0.0387	0.0273	0.0009	48	0.0226
43	43	5	5	0.0000	0.3576	44	-0.3576	45	0.0174	46	0.0032	-0.0118	-0.0387	0.0273	0.0009	49	0.0226
44	44	5	5	0.0000	0.3648	45	-0.3648	46	0.0174	47	0.0032	-0.0118	-0.0387	0.0273	0.0009	50	0.0226
45	45	5	5	0.0000	0.3720	46	-0.3720	47	0.0174	48	0.0032	-0.0118	-0.0387	0.0273	0.0009	51	0.0226
46	46	5	5	0.0000	0.3792	47	-0.3792	48	0.0174	49	0.0032	-0.0118	-0.0387	0.0273	0.0009	52	0.0226
47	47	5	5	0.0000	0.3864	48	-0.3864	49	0.0174	50	0.0032	-0.0118	-0.0387	0.0273	0.0009	53	0.0226
48	48	5	5	0.0000	0.3936	49	-0.3936	50	0.0174	51	0.0032	-0.0118	-0.0387	0.0273	0.0009	54	0.0226
49	49	5	5	0.0000	0.4008	50	-0.4008	51	0.0174	52	0.0032	-0.0118	-0.0387	0.0273	0.0009	55	0.0226
50	50	5	5	0.0000	0.4080	51	-0.4080	52	0.0174	53	0.0032	-0.0118	-0.0387	0.0273	0.0009	56	0.0226
51	51	5	5	0.0000	0.4152	52	-0.4152	53	0.0174	54	0.0032	-0.0118	-0.0387	0.0273	0.0009	57	0.0226
52	52	5	5	0.0000	0.4224	53	-0.4224	54	0.0174	55	0.0032	-0.0118	-0.0387	0.0273	0.0009	58	0.0226
53	53	5	5	0.0000	0.4296	54	-0.4296	55	0.0174	56	0.0032	-0.0118	-0.0387	0.0273	0.0009	59	0.0226
54	54	5	5	0.0000	0.4368	55	-0.4368	56	0.0174	57	0.0032	-0.0118	-0.0387	0.0273	0.0009	60	0.0226
55	55	5	5	0.0000	0.4440	56	-0.4440	57	0.0174	58	0.0032	-0.0118	-0.0387	0.0273	0.0009	61	0.0226
56	56	5	5	0.0000	0.4512	57	-0.4512	58	0.0174	59	0.0032	-0.0118	-0.0387	0.0273	0.0009	62	0.0226
57	57	5	5	0.0000	0.4584	58	-0.4584	59	0.0174	60	0.0032	-0.0118	-0.0387	0.0273	0.0009	63	0.0226
58	58	5	5	0.0000	0.4656	59	-0.4656	60	0.0174	61	0.0032	-0.0118	-0.0387	0.0273	0.0009	64	0.0226
59	59	5	5	0.0000	0.4728	60	-0.4728	61	0.0174	62	0.0032	-0.0118	-0.0387	0.0273	0.0009	65	0.0226
60	60	5	5	0.0000	0.4800	61	-0.4800	62	0.0174	63	0.0032	-0.0118	-0.0387	0.0273	0.0009	66	0.0226
61	61	5	5	0.0000	0.4872	62	-0.4872	63	0.0174	64	0.0032	-0.0118	-0.0387	0.0273	0.0009	67	0.0226
62	62	5	5	0.0000	0.4944	63	-0.4944	64	0.0174	65	0.0032	-0.0118	-0.0387	0.0273	0.0009	68	0.0226
63	63	5	5	0.0000	0.5016	64	-0.5016	65	0.0174	66	0.0032	-0.0118	-0.0387	0.0273	0.0009	69	0.0226
64	64	5	5	0.0000	0.5088	65	-0.5088	66	0.0174	67	0.0032	-0.0118	-0.0387	0.0273	0.0009	70	0.0226
65	65	5	5	0.0000	0.5160	66	-0.5160	67	0.0174	68	0.0032	-0.0118	-0.0387	0.0273	0.0009	71	0.0226
66	66	5	5	0.0000	0.5232	67	-0.5232	68	0.0174	69	0.0032	-0.0118	-0.0387	0.0273	0.0009	72	0.0226
67	67	5	5	0.0000	0.5304	68	-0.5304	69	0.0174	70	0.0032	-0.0118	-0.0387	0.0273	0.0009	73	0.0226
68	68	5	5	0.0000	0.5376	69	-0.5376	70	0.0174	71	0.0032	-0.0118	-0.0387	0.0273	0.0009	74	0.0226
69	69	5	5	0.0000	0.5448	70	-0.5448	71	0.0174	72	0.0032	-0.0118	-0.0387	0.0273	0.0009	75	0.0226
70	70	5	5	0.0000	0.5520	71	-0.5520	72	0.0174	73	0.0032	-0.0118	-0.0387	0.0273	0.0009	76	0.0226
71	71	5	5	0.0000	0.5592	72	-0.5592	73	0.0174	74	0.0032	-0.0118	-0.0387	0.0273	0.0009	77	0.0226
72	72	5	5	0.0000	0.5664	73	-0.5664	74	0.0174	75	0.0032	-0.0118	-0.0387	0.0273	0.0009	78	0.0226
73	73	5	5	0.0000	0.5736	74	-0.5736	75	0.017								

TOTAL ENERGY = -44.2170987060

1	H	BINDING ENERGY=	-3.4077704454 A.U.
2	H	0.0717	
3	C	1.0158	
4	C	4.1104	
5	H	3.0280	
6	H	1.0194	
7	O	0.0796	
8	C	6.1958	
9	H	3.4483	
10	H	1.0174	
		1.0134	

DIPOLE MOMENTS

COMPONENTS	X	Y	Z
DENSITIES	0.29894	0.01829	-0.01152
S.P	0.33343	1.14403	-0.01840
P.O	0.00000	0.00000	0.00000
TOTAL	0.63237	1.76322	-0.02831

DIPOLE MOMENT= 1.87340 DEBYES

C2

			1	2	3	4	5	6	7	8	9	10	11
1	1	H	0	0.9361	-0.0351	0.0091	0.0068	0.5410	-0.3312	0.6491	0.6474	0.0280	0.0007
2	2	H	5	-0.0361	0.9542	-0.0011	-0.0085	0.0010	-0.4166	-0.7136	-0.1102	-0.1227	0.0188
3	3	H	5	0.5001	-0.0011	0.9710	0.0069	0.0249	-0.0038	0.0263	-0.0403	-0.0705	0.5591
4	4	H	5	0.0046	-0.0089	0.0069	0.9789	0.0060	-0.0078	0.0274	-0.5213	-0.0005	0.0097
5	5	H	5	0.0018	0.0018	0.0249	0.0068	0.9582	-0.1154	-0.0289	0.0777	0.0241	-0.0013
6	6	H	5	-0.3312	-0.0166	-0.0032	-0.0070	-0.1154	0.9818	-0.0848	0.0671	0.0247	-0.0044
7	7	H	5	0.6491	-0.7136	0.1102	0.0274	-0.0060	-0.0289	0.9848	0.0178	-0.0044	0.0098
8	8	H	5	0.0046	-0.1102	-0.0403	-0.0021	0.0777	0.0671	-0.0046	1.0256	-0.0004	-0.0102
9	9	H	5	0.0280	-0.1227	-0.0705	-0.0000	0.0241	0.0247	0.0175	-0.0044	1.0036	0.0000
10	10	H	5	0.0007	0.0188	0.0091	-0.0083	-0.0013	-0.0044	-0.0044	0.0000	0.0035	-0.0099
11	11	H	5	0.0085	-0.0011	-0.7124	0.0007	0.0184	-0.0154	0.0098	-0.0182	0.0218	-0.0099
12	12	H	5	0.0068	0.0010	0.0085	0.0037	0.0064	0.0097	0.0082	-0.0181	0.0213	0.0083
13	13	H	5	0.5410	-0.0038	-0.0025	-0.0025	0.0037	0.0225	-0.0235	0.0543	-0.0044	0.0228
14	14	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
15	15	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
16	16	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
17	17	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
18	18	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
19	19	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
20	20	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
21	21	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
22	22	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
23	23	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
24	24	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
25	25	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
26	26	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
27	27	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
28	28	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
29	29	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
30	30	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
31	31	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
32	32	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
33	33	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
34	34	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
35	35	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
36	36	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
37	37	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
38	38	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
39	39	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
40	40	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
41	41	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
42	42	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
43	43	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
44	44	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
45	45	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
46	46	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
47	47	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
48	48	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
49	49	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
50	50	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
51	51	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
52	52	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
53	53	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
54	54	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
55	55	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
56	56	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
57	57	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
58	58	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
59	59	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082
60	60	H	5	0.0018	0.0018	0.0080	0.1803	0.0125	0.3679	-0.1013	0.0772	0.0389	-0.0082

1	1	H	S	12	13	14	15	16	17	18	19	20	21	22
				-0.0037	-0.0018	-0.0018	-0.0018	-0.0018	-0.0018	-0.0018	-0.0018	-0.0018	-0.0018	-0.0018
2	2	H	S	-0.0044	-0.0213	-0.0211	-0.0271	-0.0071	-0.0021	-0.0000	-0.0221	-0.0010	-0.0014	-0.0032
3	3	H	S	0.2442	-0.2020	-0.0000	-0.0000	-0.0014	-0.0010	-0.0435	-0.0224	-0.0209	-0.0124	-0.0126
4	4	H	S	0.0037	-0.0254	0.0523	0.2284	-0.7012	-0.1763	0.0130	0.0090	-0.0063	0.0442	-0.0083
5	5	H	S	0.0004	-0.0037	0.2160	-0.3740	0.0360	0.0100	0.1703	0.0395	-0.1536	0.3233	-0.0003
6	6	H	S	0.0007	-0.0225	0.3079	-0.6160	0.0040	-0.0017	0.0746	0.0766	-0.1320	0.0000	-0.0000
7	7	H	S	-0.0002	-0.0236	-0.1013	-0.2307	0.1461	-0.0352	0.1460	0.0523	-0.0270	0.3097	-0.0004
8	8	H	S	-0.0131	-0.0063	0.0772	-0.2002	-0.0126	0.1527	0.2056	-0.0047	-0.2577	-0.3770	-0.0001
9	9	H	S	0.0213	-0.0046	0.0164	-0.0056	-0.0210	0.0560	0.4191	-0.5364	-0.5631	-0.3040	-0.0036
10	10	H	S	0.0003	0.0220	0.0132	-0.0030	0.0060	0.0164	0.3033	-0.1334	-0.0300	-0.0000	-0.0000
11	11	H	S	0.0045	-0.0101	-0.0015	0.0236	0.0083	-0.0156	0.0056	0.4330	0.1405	-0.0577	-0.0120
12	12	H	S	0.0023	-0.0364	-0.0268	0.0052	-0.0053	0.0144	-0.0076	0.0137	-0.1570	-0.0046	-0.0030
13	13	H	S	-0.0034	1.4077	0.0256	-0.0301	-0.0140	-0.0104	0.0005	-0.0072	-0.0041	0.1500	-0.0001
14	14	H	S	-0.0006	0.0256	0.0610	0.0725	-0.0075	0.0037	0.0061	-0.0066	0.0163	-0.0256	-0.0004
15	15	H	S	0.0032	-0.0361	0.0725	0.0933	0.0060	-0.1302	0.0000	0.0283	0.0056	0.0104	-0.0007
16	16	H	S	-0.0053	-0.0166	-0.0075	0.0060	0.0700	-0.0324	-0.0000	0.0133	-0.0077	-0.0002	-0.0000
17	17	H	S	0.0146	0.0164	0.0037	-0.1302	-0.0324	0.0031	-0.0023	-0.0233	-0.0110	0.0120	-0.0016
18	18	H	S	0.4076	-0.0050	0.0001	0.0000	-0.0000	-0.0023	0.0033	-0.1700	0.1181	-0.0040	0.0101
19	19	H	S	0.2137	-0.0072	-0.0066	0.0243	0.0133	-0.0233	-0.1700	0.0205	-0.0000	-0.0000	-0.0010
20	20	H	S	-0.0000	-0.0001	0.0163	0.0006	0.0077	-0.0110	0.1181	-0.0000	1.0030	0.0176	0.0201
21	21	H	S	-0.0046	0.3000	-0.0256	0.0104	-0.0262	0.0120	-0.0000	-0.0022	0.0176	0.0492	0.0030
22	22	H	S	-0.0039	0.0051	-0.0004	-0.0007	-0.0000	0.0010	0.0101	-0.0010	0.0261	0.0030	1.7700
23	23	H	S	0.0039	0.1256	-0.0000	-0.0110	-0.0000	0.0101	-0.0010	-0.0175	-0.0376	0.0201	0.0750
24	24	H	S	0.0004	0.0239	0.0007	0.0110	0.0110	-0.0223	-0.0005	0.0110	-0.0000	-0.0000	0.0320
25	25	H	S	0.0011	-0.0003	-0.0000	0.0000	-0.0003	0.0031	-0.0003	-0.0001	-0.0015	-0.0007	0.0000
26	26	H	S	0.3343	0.1502	0.0183	0.0130	0.0160	-0.0240	0.0141	0.0053	0.0270	-0.0062	0.2307
27	27	H	S	-0.0000	-0.0151	0.0135	0.0212	0.0240	-0.0292	-0.0062	-0.0226	0.0137	-0.0233	0.0004
28	28	H	S	-0.0707	-0.1375	-0.0107	-0.0102	-0.0105	0.0340	-0.0022	-0.0234	-0.0044	-0.0017	0.3030
29	29	H	S	-0.1702	0.5106	0.0066	0.0006	0.0020	-0.0006	-0.0000	-0.0317	-0.0077	0.0211	0.0301
30	30	H	S	-0.0044	0.0160	0.2642	0.0360	0.3100	-0.3452	0.1342	0.2063	-0.0074	0.0356	0.0143
31	31	H	S	0.0349	0.0073	0.1170	0.3000	0.1900	-0.2760	-0.2500	0.3300	0.0050	-0.0047	-0.0030
32	32	H	S	0.0155	0.0040	-0.1700	0.0420	-0.1220	0.1070	0.0053	0.0021	0.0005	0.0320	0.0112
33	33	H	S	0.0106	-0.0094	0.2363	0.0363	0.3000	-0.1630	-0.0700	-0.1400	0.0066	0.0050	0.0031
34	34	H	S	-0.0000	0.0430	-0.0070	0.0004	0.0043	0.0177	0.1301	0.2330	-0.0054	-0.1770	0.0007
35	35	H	S	0.0140	-0.1530	0.0030	-0.0130	-0.0042	0.0700	-0.2017	-0.0533	0.1073	0.0760	0.0000
36	36	H	S	0.0041	0.0202	0.0000	0.0207	0.0363	-0.0046	0.0207	0.1190	0.0005	-0.0027	-0.0030
37	37	H	S	-0.0004	-0.0031	-0.0376	-0.0053	-0.0361	0.0040	0.1300	0.2047	-0.0007	-0.0711	0.0000
38	38	H	S	0.0022	-0.0015	-0.1655	0.1632	0.1557	0.3204	0.0140	0.0124	-0.0127	0.0176	-0.0000
39	39	H	S	-0.0024	0.0106	-0.0106	-0.0147	0.1326	-0.3031	-0.0100	-0.0077	0.0151	-0.0216	0.0010
40	40	H	S	-0.0024	0.0060	-0.1700	-0.1302	0.0026	0.2937	0.0113	-0.0000	-0.0000	-0.0000	-0.0000
41	41	H	S	-0.0000	-0.0000	-0.3671	-0.3117	-0.2434	-0.0490	-0.0206	-0.0207	0.0140	-0.0220	0.0011
42	42	H	S	0.0110	-0.0200	-0.0030	-0.0063	-0.0130	0.0075	-0.0360	0.0230	-0.0082	-0.0090	-0.0046
43	43	H	S	0.0127	0.0235	0.0004	-0.0000	-0.0130	0.0311	0.0005	-0.0121	0.0116	0.0410	-0.0120
44	44	H	S	-0.0207	0.0000	0.0170	0.0226	0.0130	-0.0010	-0.0200	-0.0330	-0.0127	-0.1560	-0.0104
45	45	H	S	0.0102	-0.0001	-0.0000	0.0000	0.0007	0.0006	0.0051	0.0000	0.0320	-0.0757	-0.0045
46	46	H	S	-0.0005	-0.0010	0.0220	0.0310	-0.0030	0.0051	-0.0007	-0.0002	0.0000	-0.0020	-0.0002
47	47	H	S	0.0000	0.0030	-0.0232	-0.0150	0.0233	-0.0376	-0.0000	-0.0004	-0.0002	-0.0003	-0.0000
48	48	H	S	-0.0012	0.0005	0.0104	0.0001	0.0000	-0.0000	-0.0031	-0.0031	0.0034	-0.0007	0.0001
49	49	H	S	0.0004	0.0010	-0.0356	-0.0470	0.0432	-0.0053	0.0014	0.0000	-0.0000	0.0015	0.0000
50	50	H	S	-0.0013	0.0016	-0.0244	-0.0103	-0.0170	-0.0200	-0.0020	-0.0010	0.0020	-0.0000	0.0000
51	51	H	S	0.0043	0.0206	0.0000	-0.0021	0.0033	0.0004	-0.0023	-0.0040	-0.0020	0.0005	0.0000
52	52	H	S	-0.0176	-0.0147	-0.0001	-0.0102	-0.0063	0.0200	0.0223	0.0160	0.0066	0.0102	-0.0101
53	53	H	S	-0.0000	-0.0000	0.0000	0.0000	0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000
54	54	H	S	-0.0000	-0.0000	0.0000	0.0000	0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000
55	55	H	S	-0.0000	-0.0000	0.0000	0.0000	0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000
56	56	H	S	-0.0114	-0.0004	0.0000	0.0000	0.0000	-0.0000	-0.0000	0.0001	-0.0073	0.0063	0.0063
57	57	H	S	-0.0000	0.0004	-0.0152	-0.0001	0.0004	0.0001	-0.0010	-0.0013	0.0007	-0.0020	-0.0001
58	58	H	S	0.0001	-0.0016	0.0743	0.0417	0.0120	0.0000	0.0007	0.0040	-0.0067	-0.0000	-0.0001
59	59	H	S	0.0000	-0.0107	-0.0072	0.0123	0.0010	-0.0010	-0.0032	0.0020	0.0062	-0.0107	-0.0000

1	I	H	S	-0.0021	0.0145	0.0008	0.0063	0.0021	-0.0109	0.0011	0.0244	-0.0401	-0.0325	-0.0157
2	2	H	S	-0.0056	-0.0072	-0.0045	0.0049	0.0047	-0.0068	0.0007	0.0173	0.1041	0.0006	-0.0002
3	3	H	S	0.0158	0.0276	0.0141	-0.0352	0.0502	0.0080	-0.0003	0.0262	-0.0020	-0.0138	-0.0058
4	4	H	S	0.0048	-0.0142	0.0004	-0.0086	-0.0034	0.0129	-0.0106	-0.0165	-0.0061	0.0326	-0.0152
5	5	C	S	-0.0145	-0.0043	0.0041	-0.0103	0.0158	0.0108	-0.0503	0.1243	-0.0258	-0.0525	0.1646
6	6	S	PH	0.0009	0.0007	-0.0004	-0.0008	-0.0030	-0.0017	0.0146	0.1072	-0.0101	-0.1372	0.1664
7	7	S	PH	-0.0128	-0.0104	0.0304	-0.0144	0.0183	0.0170	-0.0388	0.0777	-0.0251	0.0378	0.1419
8	8	C	PH	0.0140	0.0033	0.0611	0.0142	0.0150	-0.0129	0.0621	-0.0861	0.2068	-0.0787	-0.0015
9	9	H	S	0.0250	0.0277	0.0015	0.0402	-0.0510	-0.0503	-0.0103	0.0118	0.0920	0.0148	-0.0515
10	10	C	S	0.0094	0.0287	0.0185	0.3873	-0.3861	-0.2422	-0.1346	0.0012	-0.0027	-0.0213	-0.0151
11	11	C	PH	0.0075	0.0246	0.1214	0.3761	-0.1631	-0.2781	0.3220	-0.0135	-0.0531	0.0081	0.0187
12	12	C	PH	0.0395	0.0084	0.0611	0.3343	-0.2609	-0.0707	-0.1782	-0.0404	0.0349	-0.0155	0.0104
13	13	C	PH	0.1256	0.0238	-0.2083	0.1582	-0.3151	-0.1375	0.5106	0.0180	0.0673	0.0080	-0.0594
14	14	C	S	-0.0000	0.0007	-0.0094	0.0163	0.0135	-0.0107	0.0000	0.2582	0.1170	-0.2708	0.2363
15	15	C	PH	-0.0019	0.0119	-0.0028	0.0130	0.0212	-0.0198	0.0009	0.0360	0.2268	-0.0426	-0.0303
16	16	C	PH	-0.0019	0.0119	-0.0028	0.0130	0.0212	-0.0198	0.0009	0.0360	0.2268	-0.0426	-0.0303
17	17	C	PH	0.0161	-0.0223	0.0031	-0.0248	-0.0292	0.0340	-0.0008	-0.3452	-0.2746	0.4078	-0.1635
18	18	C	S	-0.0251	-0.0505	-0.0053	0.0141	-0.0092	-0.0022	-0.0040	0.1342	-0.2584	-0.0053	-0.0780
19	19	C	PH	0.0175	0.0119	0.0341	0.0053	-0.0220	-0.0234	-0.0317	0.0383	-0.1308	0.0021	-0.1400
20	20	C	PH	0.0370	-0.0490	-0.0015	0.0270	0.0137	-0.0404	-0.0077	-0.0074	0.0458	0.0055	0.0049
21	21	C	PH	0.0281	-0.0057	-0.0407	-0.0062	0.0233	-0.0017	0.0211	0.0386	-0.0247	0.0325	0.0950
22	22	C	S	0.0755	0.4320	0.0450	0.2367	0.0004	0.3034	0.1081	0.0143	-0.0030	0.0212	0.0031
23	23	C	PH	1.6821	-0.1295	0.0806	-0.0378	0.3077	-0.1956	-0.1433	0.0112	0.0344	0.0090	0.0077
24	24	C	PH	-0.1295	-1.1678	-0.0684	-0.0445	0.1510	-0.8389	-0.1838	-0.0046	-0.0535	-0.0622	-0.0187
25	25	C	PH	0.0008	-0.0044	1.8733	-0.0300	-0.1421	0.1201	0.5937	-0.0003	0.0015	0.0221	0.0071
26	26	C	S	-0.0376	-0.0445	-0.0394	1.0468	0.0031	0.1088	-0.0270	0.0091	0.0094	0.0127	0.0005
27	27	C	PH	0.1077	-0.1510	-0.1421	-0.0831	0.8562	0.0868	0.0315	0.0024	0.0420	0.0142	-0.0014
28	28	C	PH	-0.1376	-0.0450	-0.1201	0.1088	0.0080	0.9302	0.0376	-0.0057	0.0254	0.0087	0.0110
29	29	C	PH	-0.1433	-0.0158	0.5637	-0.0270	0.0315	0.0376	0.0031	0.0181	0.0127	-0.0148	-0.0011
30	30	C	S	0.0112	-0.0546	-0.0003	0.0001	0.0204	0.0057	0.0181	0.0777	0.2254	0.0470	0.0344
31	31	C	PH	0.0344	-0.0135	-0.0015	0.0096	0.0409	0.0254	0.0127	0.0254	0.7040	-0.0742	0.0202
32	32	C	PH	0.0009	-0.0022	0.0221	0.0127	0.0142	-0.0087	0.0148	0.0470	-0.0742	0.0430	0.0323
33	33	C	PH	0.0077	-0.0147	0.0071	0.0005	0.0014	0.0110	-0.0111	0.0344	0.0092	0.0323	0.0762
34	34	C	S	0.0085	-0.0027	-0.0308	-0.0130	-0.0084	0.0099	0.2351	0.1819	-0.0265	-0.0041	-0.2155
35	35	C	PH	0.0223	0.0074	0.0595	0.0196	0.0200	-0.0146	-0.0773	0.1501	0.1870	0.0065	-0.3214
36	36	C	PH	0.0066	0.0068	0.0238	-0.0130	-0.0078	0.0091	0.0320	0.0700	-0.0312	0.0087	-0.1474
37	37	C	PH	0.0106	-0.0097	-0.0348	-0.0250	-0.0160	0.0160	0.0452	0.1340	-0.0040	-0.1057	-0.0106
38	38	C	S	-0.0047	0.0042	0.0033	-0.0002	0.0042	-0.0028	-0.0030	-0.0185	0.0126	0.0223	-0.0052
39	39	C	PH	0.0055	-0.0089	-0.0031	-0.0053	-0.0090	0.0075	0.0028	-0.0197	-0.0044	0.0020	-0.0055
40	40	C	PH	0.0038	-0.0050	-0.0021	-0.0010	0.0014	0.0032	0.0000	-0.0280	-0.0137	0.0308	-0.0050
41	41	C	PH	0.0039	-0.0040	-0.0030	0.0025	-0.0034	0.0004	0.0044	0.0423	0.0435	-0.0103	-0.0142
42	42	C	S	-0.0401	0.0708	-0.0700	0.2348	0.3785	-0.2720	0.1548	0.0282	0.0634	0.0490	0.0931
43	43	C	PH	0.0572	-0.0305	0.0700	-0.2411	-0.2470	0.2013	-0.2170	-0.0088	0.1808	-0.0023	-0.0608
44	44	C	PH	-0.0701	0.0241	-0.0133	0.2434	0.3463	-0.1470	0.1107	-0.0484	-0.1380	-0.0153	-0.1661
45	45	C	PH	0.1019	-0.0107	-0.1204	-0.1093	0.2452	0.1214	0.2211	-0.0040	-0.1368	-0.1598	0.1801
46	46	C	S	0.0001	0.0004	-0.0007	0.0012	0.0004	-0.0005	-0.0005	0.0283	0.0134	-0.0211	0.0103
47	47	C	PH	0.0002	-0.0006	0.0003	-0.0014	0.0014	0.0003	0.0003	-0.0243	-0.0195	0.0210	-0.0119
48	48	C	PH	0.0014	-0.0005	-0.0017	0.0007	-0.0008	0.0000	0.0012	0.0290	0.0116	-0.0151	0.0158
49	49	C	PH	-0.0010	0.0003	0.0006	-0.0001	0.0005	-0.0004	-0.0005	-0.0228	-0.0048	0.0154	-0.0121
50	50	C	S	0.0001	0.0000	-0.0009	0.0000	0.0004	-0.0007	0.0010	0.0128	0.0032	-0.0103	0.0006
51	51	H	S	-0.0091	0.0027	0.0252	-0.0090	0.0038	0.0057	0.0027	0.0538	0.0284	0.0010	-0.0027
52	52	C	S	0.0092	0.0174	0.0148	0.0103	-0.0027	-0.0015	-0.0072	-0.0069	0.0301	0.0115	-0.0036
53	53	C	PH	-0.0134	-0.0147	-0.0221	-0.0044	-0.0093	0.0124	0.0157	-0.0447	0.0047	0.0118	0.0068
54	54	C	PH	-0.0103	0.0012	-0.0000	0.0031	0.0330	-0.0002	0.0007	-0.0007	-0.0007	-0.0170	-0.0005
55	55	C	PH	0.0003	-0.0038	-0.0240	-0.0045	-0.0041	-0.0023	0.0008	0.0034	-0.0205	0.0002	0.0050
56	56	C	S	-0.0066	-0.0027	-0.0045	0.0434	0.0650	-0.0342	0.0228	-0.0494	0.0045	-0.0041	-0.0167
57	57	C	S	-0.0002	0.0067	-0.0005	0.0009	0.0005	-0.0010	0.0005	0.0040	0.0075	0.0078	0.0035
58	58	C	S	-0.0004	-0.0001	0.0016	-0.0015	-0.0002	0.0011	-0.0016	-0.0200	-0.0121	0.0177	-0.0096
59	59	C	S	0.0167	0.0013	-0.0253	-0.0115	-0.0277	0.0130	0.0200	0.0301	-0.0172	0.0285	0.0310

			34	35	36	37	38	39	40	41	42	43	44
1	1	H	S	-0.0281	-0.0540	0.0043	0.0676	-0.0311	0.0284	0.0236	0.0090	-0.0106	0.0060
2	2	H	S	-0.0047	-0.0710	0.0020	-0.0284	0.0246	-0.0246	-0.0177	-0.0376	0.0233	-0.0263
3	3	H	S	0.0194	-0.0310	0.0024	0.0287	0.0041	-0.0036	-0.0020	-0.0063	0.0087	-0.0066
4	4	H	S	-0.0110	-0.0271	-0.0111	-0.0476	0.0106	-0.0344	0.0136	0.0314	0.0394	-0.0153
5	5	C	S	0.0088	0.0476	0.0260	-0.0467	-0.0076	0.0507	-0.0023	-0.0160	-0.0090	0.0263
6	5	C	PK	0.0013	0.0460	0.0071	0.0207	-0.0046	0.0737	0.0053	-0.0243	0.0110	0.0080
7	5	C	PV	0.0132	0.0502	0.0075	-0.0487	-0.0130	-0.0356	-0.0115	0.0208	-0.0163	0.0125
8	6	C	PZ	0.0065	-0.0332	0.0213	0.0053	-0.0180	0.0350	0.0020	-0.0137	0.0015	-0.0303
9	6	H	S	-0.0164	0.0450	0.0061	0.0291	-0.0021	0.0248	0.0070	-0.0106	0.0371	-0.0440
10	7	C	S	0.0041	-0.0085	-0.0364	0.0109	0.0008	-0.0010	-0.0011	0.0008	-0.0246	0.0137
11	7	C	PK	-0.0284	0.0420	0.0131	-0.0178	0.0000	-0.0061	-0.0025	0.0015	-0.0174	-0.0137
12	7	C	PV	-0.0069	0.0186	0.0461	-0.0044	0.0022	-0.0024	-0.0024	-0.0050	0.0110	0.0127
13	7	C	PZ	0.0430	-0.1520	0.0202	0.0051	-0.0015	0.0109	0.0044	-0.0006	-0.0280	0.0236
14	8	C	S	-0.0078	0.0036	0.0400	-0.0374	0.1055	-0.1060	-0.1760	-0.3071	0.0030	0.0004
15	8	C	PK	0.0004	-0.1314	0.0207	-0.0053	0.1033	-0.0147	-0.1552	-0.3117	-0.0063	0.0224
16	8	C	PV	0.0043	-0.0442	0.0363	-0.0361	0.1937	-0.1320	0.0026	-0.2434	-0.0130	-0.0136
17	8	C	PZ	0.0177	0.0745	-0.0404	0.0450	0.3264	-0.3051	-0.2637	-0.4406	0.0075	0.0311
18	8	C	S	-0.1351	-0.2487	0.0257	0.1380	0.0140	-0.0186	-0.0113	-0.0200	0.0336	-0.0465
19	8	C	PK	0.2335	-0.4333	0.1100	0.2047	0.0124	-0.0077	-0.0080	-0.0207	0.0230	-0.0121
20	8	C	PV	-0.0056	0.1073	0.0005	-0.0537	-0.0127	0.0151	0.0088	0.0166	0.0782	0.0118
21	8	C	PZ	-0.1770	0.4748	-0.0621	-0.0711	0.0176	-0.0218	-0.0180	-0.0220	-0.0080	0.0410
22	10	O	S	-0.0007	-0.0000	-0.0030	0.0012	-0.0008	0.0010	0.0009	0.0011	-0.0040	-0.0120
23	10	O	PK	0.0080	-0.0223	0.0060	0.0100	-0.0047	0.0055	0.0036	0.0038	-0.1401	0.0372
24	10	O	PV	-0.0027	0.0376	0.0008	-0.0087	0.0042	-0.0064	0.0050	-0.0040	0.0786	-0.0305
25	10	O	PZ	-0.0300	0.0505	-0.0030	-0.0348	0.0033	-0.0031	-0.0021	-0.0030	-0.0700	0.0700
26	11	C	S	-0.0136	0.0100	-0.0130	-0.0250	-0.0002	-0.0053	-0.0010	0.0025	0.2348	-0.2011
27	11	C	PK	-0.0084	0.0200	-0.0070	-0.0100	0.0052	-0.0050	-0.0034	0.0034	0.3700	-0.3453
28	11	C	PV	0.0009	-0.0146	0.0091	0.0100	-0.0028	0.0075	0.0032	0.0004	-0.2720	0.2913
29	11	C	PZ	0.0351	-0.0751	0.0325	0.0452	-0.0030	0.0020	0.0006	0.0044	0.1500	-0.1470
30	12	C	S	0.0108	0.1501	0.0706	0.0640	-0.0180	-0.0187	-0.0080	0.0423	0.2012	-0.0006
31	12	C	PK	-0.0135	0.1070	-0.0312	-0.0060	-0.0126	-0.0044	-0.0137	0.0433	0.0034	0.1808
32	12	C	PV	-0.0041	-0.0045	0.0097	0.1657	0.0023	0.0299	0.0326	-0.0313	0.0100	-0.0023
33	12	C	PZ	-0.3189	-0.3214	-0.1474	-0.0100	0.0032	-0.0030	-0.0000	0.0132	0.0031	-0.0060
34	13	O	S	1.0093	0.1341	-0.1155	-0.0543	0.0125	-0.0006	-0.0032	-0.0235	-0.0015	-0.0017
35	13	O	PK	0.1341	1.4300	0.0580	0.0370	0.0157	0.0184	0.0000	-0.0350	0.0130	-0.0042
36	13	O	PV	-0.1155	0.0080	1.0271	-0.1773	-0.0000	-0.0065	-0.0000	0.0025	-0.0500	0.0100
37	13	O	PZ	-0.0454	0.0370	0.1773	1.2070	0.0347	-0.0187	-0.0107	-0.0050	-0.0011	-0.0132
38	14	O	S	0.0122	0.0157	-0.0006	0.0347	1.0096	0.0250	0.0378	0.1101	-0.0109	-0.0006
39	14	O	PK	-0.0080	0.0186	-0.0000	0.0187	0.0250	1.1705	0.0434	-0.3213	0.0114	0.0040
40	14	O	PV	-0.0032	0.0000	-0.0000	-0.0107	0.4378	0.0434	1.4380	-0.0077	0.0004	-0.0002
41	14	O	PZ	-0.0035	-0.0000	0.0025	-0.0503	0.1101	-0.3213	0.0097	1.3010	0.0073	-0.0005
42	15	H	S	-0.0015	0.0130	-0.0000	0.0011	-0.0100	0.0116	0.0094	0.0273	1.2000	-0.0070
43	15	H	PK	-0.0017	-0.0042	0.0100	-0.0132	-0.0000	0.0048	-0.0002	-0.0000	-0.0070	1.2070
44	15	H	PV	0.0000	-0.0000	0.0021	0.0037	0.0261	-0.0287	-0.0280	-0.0074	0.1230	-0.0361
45	15	H	PZ	0.0000	0.1143	0.0322	0.0003	-0.0000	-0.0094	0.0012	0.0074	0.0072	-0.1762
46	16	C	S	-0.0016	-0.0047	0.0702	-0.0076	0.1020	0.1075	-0.3142	0.2757	0.0000	0.0001
47	16	C	PK	0.0025	0.0084	-0.0010	0.0003	-0.1017	0.0357	0.2729	-0.1920	-0.0024	0.0011
48	16	C	PV	-0.0029	-0.0053	0.0010	-0.0014	0.3180	0.2455	-0.3500	0.3374	0.0003	-0.0002
49	16	C	PZ	0.0030	0.0023	0.0002	0.0000	-0.2303	-0.0424	0.3034	-0.1062	-0.0037	-0.0000
50	17	H	S	-0.0017	-0.0000	0.0011	-0.0002	0.0071	0.1000	0.0060	-0.0172	0.0000	-0.0003
51	18	H	S	-0.0000	-0.0100	-0.0171	-0.0047	0.0028	0.0036	0.0044	0.0300	0.0390	-0.0026
52	19	C	S	0.0034	-0.0100	0.0091	0.0002	-0.0000	-0.0012	0.0030	0.0000	0.2530	0.3605
53	19	C	PK	-0.0075	0.0134	-0.0173	-0.0100	-0.0130	-0.0120	-0.0074	0.0155	-0.0028	-0.0033
54	19	C	PV	-0.0045	0.0004	0.0010	-0.0003	0.0051	-0.0003	-0.0017	-0.0011	-0.1076	-0.2350
55	19	C	PZ	0.0020	0.0121	0.0005	0.0000	-0.0012	0.0001	0.0110	0.0007	-0.1212	-0.1990
56	20	H	S	0.0023	-0.0010	0.0130	0.0050	0.0017	0.0072	0.0077	-0.0000	0.0153	-0.0283
57	21	H	S	-0.0000	-0.0025	0.0011	-0.0015	0.0102	-0.1041	0.0213	0.0756	-0.0004	0.0000
58	22	H	S	0.0044	0.0047	-0.0024	0.0131	-0.0300	0.0058	-0.0202	-0.0071	-0.0020	0.0000
59	23	H	S	0.0037	0.0222	-0.0031	0.0100	0.0100	0.0040	0.0075	-0.0010	0.0004	-0.0257

				45	46	47	48	49	50	51	52	53	54	55
1	1	H	8	0.0100	0.0010	-0.0039	0.0070	-0.0047	0.0004	-0.0011	-0.0011	-0.0011	0.0013	-0.0013
2	2	H	5	0.0054	0.0017	0.0006	-0.0018	0.0001	-0.0001	0.0007	-0.0127	0.0192	0.0116	0.0001
3	3	H	5	-0.0034	-0.0007	0.0002	-0.0017	0.0006	-0.0000	-0.0002	-0.0107	0.0277	0.0136	0.0005
4	4	H	5	0.0045	-0.0070	0.0152	-0.0425	0.0036	-0.0000	0.0033	-0.0003	0.0026	0.0006	0.0010
5	5	C	8	-0.0041	0.0075	0.0012	0.0128	-0.0144	0.0000	-0.0002	0.0147	-0.0107	-0.0137	-0.0006
6	5	C	PK	-0.0010	0.0117	0.0005	0.0174	-0.0194	0.0113	0.0019	0.0099	-0.0005	-0.0004	-0.0071
7	5	C	PK	-0.0021	0.0040	0.0007	0.0001	-0.0012	-0.0033	0.0027	0.0113	-0.0108	-0.0023	-0.0009
8	5	C	PZ	-0.0010	0.0000	0.0077	0.0002	0.0002	0.0001	0.0042	-0.0163	0.0024	-0.0142	-0.0070
9	6	H	8	0.0147	-0.0011	0.0040	0.0000	-0.0000	0.0010	0.0044	-0.0110	0.0222	0.0102	0.0000
10	7	C	8	0.0023	0.0000	0.0007	0.0000	-0.0000	0.0000	0.0007	0.0040	-0.0390	-0.0124	-0.0103
11	7	C	PK	0.0348	0.0010	0.0017	0.0005	-0.0000	-0.0000	0.0001	-0.0337	-0.0178	-0.0010	0.0010
12	7	C	PZ	-0.0142	-0.0005	0.0000	-0.0012	0.0000	-0.0013	0.0003	0.0110	-0.0170	-0.0050	-0.0020
13	7	C	PZ	-0.0107	-0.0013	0.0030	0.0005	-0.0010	0.0010	0.0010	0.0125	-0.0147	-0.0004	-0.0100
14	8	C	5	-0.0412	0.0220	-0.0252	0.0184	-0.0350	-0.0344	0.0046	-0.0030	0.0001	-0.0005	-0.0002
15	8	C	PK	0.0000	0.0315	-0.0150	0.0001	-0.0470	-0.0183	-0.0021	-0.0102	0.0021	0.0124	0.0102
16	8	C	PZ	0.0007	-0.0010	0.0033	0.0000	0.0032	-0.0174	0.0033	-0.0003	0.0007	0.0002	0.0007
17	8	C	PZ	0.0000	0.0041	-0.0304	-0.0002	-0.0053	-0.0200	0.0000	0.0000	-0.0100	-0.0153	0.0000
18	9	C	8	0.0051	-0.0007	0.0005	-0.0031	0.0014	-0.0020	-0.0023	0.0023	-0.0316	-0.0183	-0.0001
19	9	C	PK	0.0000	-0.0002	-0.0000	-0.0031	0.0000	-0.0010	-0.0000	0.0100	-0.0172	-0.0000	-0.0002
20	9	C	PZ	0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	0.0000	0.0000	-0.0000	-0.0000
21	9	C	PZ	-0.0073	-0.0002	0.0000	-0.0000	0.0010	-0.0000	0.0000	0.0100	-0.0020	-0.0010	-0.0002
22	10	D	5	-0.0045	-0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0100	-0.0020	-0.0010	-0.0002
23	10	D	PK	0.0109	0.0001	0.0002	0.0001	0.0000	0.0000	0.0000	0.0100	0.0043	0.0001	0.0007
24	10	D	PZ	-0.0107	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0100	-0.0100	-0.0000	-0.0000
25	10	D	PZ	-0.0107	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0100	-0.0100	-0.0000	-0.0000
26	11	C	5	-0.1003	0.0012	-0.0014	0.0007	-0.0001	0.0000	-0.0000	0.0100	-0.0100	0.0001	-0.0000
27	11	C	PK	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0100	-0.0100	0.0001	-0.0000
28	11	C	PZ	-0.0100	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0100	-0.0100	0.0001	-0.0000
29	11	C	PZ	0.0011	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0100	-0.0100	0.0001	-0.0000
30	12	C	8	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0100	-0.0100	0.0001	-0.0000
31	12	C	PK	-0.0100	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0100	-0.0100	0.0001	-0.0000
32	12	C	PZ	-0.0100	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0100	-0.0100	0.0001	-0.0000
33	12	C	PZ	-0.0100	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0100	-0.0100	0.0001	-0.0000
34	13	D	5	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0100	-0.0100	0.0001	-0.0000
35	13	D	PK	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0100	-0.0100	0.0001	-0.0000
36	13	D	PZ	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0100	-0.0100	0.0001	-0.0000
37	14	D	5	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0100	-0.0100	0.0001	-0.0000
38	14	D	PK	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0100	-0.0100	0.0001	-0.0000
39	14	D	PZ	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0100	-0.0100	0.0001	-0.0000
40	14	D	PZ	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0100	-0.0100	0.0001	-0.0000
41	15	H	5	0.0072	0.0000	0.0000	0.0043	-0.0037	0.0000	-0.0000	0.0000	0.0000	-0.0000	-0.0000
42	15	H	PK	-0.0100	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
43	15	H	PZ	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
44	15	H	PZ	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
45	15	H	PZ	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
46	16	C	8	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
47	16	C	PK	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
48	16	C	PZ	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
49	16	C	PZ	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
50	17	H	5	-0.0003	0.0100	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
51	17	H	PK	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
52	17	H	PZ	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
53	17	H	PZ	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
54	20	H	5	-0.0170	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
55	21	H	5	-0.0003	0.0113	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
56	22	H	5	0.0012	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
57	23	H	5	-0.0003	-0.0003	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

1	1	H	S	0.0084	0.0098	-0.0108	-0.0017
2	2	H	S	-0.0099	0.0039	0.0034	0.0149
3	3	H	S	0.0178	-0.0006	0.0020	-0.0009
4	4	H	S	-0.0099	0.0047	0.0284	0.0110
5	5	C	S	0.0098	0.0050	-0.0045	-0.0114
6	5	C	PR	0.0053	-0.0001	-0.0082	-0.0064
7	5	C	PY	0.0026	0.0015	-0.0009	-0.0432
8	6	C	PZ	-0.0081	-0.0014	0.0092	0.0068
9	8	H	S	-0.0076	-0.0018	0.0004	0.0117
10	7	C	S	-0.0067	0.0004	-0.0010	0.0013
11	7	C	PK	-0.0080	0.0002	0.0000	0.0105
12	7	C	PY	-0.0141	-0.0004	0.0021	0.0088
13	7	C	PZ	-0.0064	0.0004	-0.0014	-0.0167
14	8	C	S	0.0098	-0.0152	0.0743	-0.0072
15	8	C	PR	0.0084	-0.0061	0.0417	0.0123
16	8	C	PY	0.0073	0.0084	0.0136	0.0019
17	8	C	PZ	-0.0098	0.0001	0.0640	-0.0019
18	9	C	S	-0.0099	-0.0010	0.0057	-0.0032
19	9	C	PR	0.0081	-0.0013	0.0046	0.0020
20	9	C	PY	-0.0073	0.0007	-0.0047	0.0024
21	9	C	PZ	0.0043	-0.0025	0.0090	-0.0167
22	10	D	S	0.0083	-0.0001	0.0001	-0.0004
23	10	D	PR	-0.0084	-0.0002	-0.0004	0.0197
24	10	D	PY	-0.0027	0.0007	-0.0001	0.0013
25	10	D	PZ	-0.0045	-0.0005	0.0010	-0.0253
26	11	C	S	0.0434	0.0009	-0.0015	-0.0119
27	11	C	PR	0.0050	0.0005	-0.0002	-0.0217
28	11	C	PY	-0.0342	-0.0010	0.0011	0.0139
29	11	C	PZ	0.0228	0.0005	-0.0016	0.0080
30	12	C	S	-0.0494	0.0000	-0.0200	0.0301
31	12	C	PR	0.0045	0.0075	-0.0121	-0.0172
32	12	C	PY	-0.0561	-0.0078	0.0177	0.0085
33	12	C	PZ	-0.0167	0.0035	-0.0090	0.0310
34	13	D	S	0.0023	-0.0004	0.0044	0.0037
35	13	D	PR	-0.0019	-0.0025	0.0047	0.0022
36	13	D	PY	0.0130	0.0011	-0.0024	-0.0031
37	13	D	PZ	0.0050	-0.0010	0.0131	0.0109
38	14	D	S	0.0017	0.0102	-0.0368	0.0100
39	14	D	PR	0.0072	-0.0041	0.0050	0.0048
40	14	D	PY	0.0077	0.0213	-0.0282	0.0075
41	14	D	PZ	-0.0066	0.0756	-0.0571	-0.0016
42	15	H	S	0.0153	-0.0004	-0.0026	0.0004
43	15	H	PR	-0.0263	0.0000	0.0009	-0.0257
44	15	H	PY	0.0376	0.0017	0.0033	-0.0222
45	15	H	PZ	-0.0170	-0.0003	0.0012	0.1203
46	16	C	S	0.0057	0.0113	0.4087	-0.0025
47	16	C	PR	-0.0023	0.0010	0.1787	0.0030
48	16	C	PY	0.0080	-0.0271	0.3299	-0.0036
49	16	C	PZ	-0.0059	-0.0709	0.7669	0.0031
50	17	H	S	0.0063	-0.0409	-0.0378	0.0010
51	18	H	S	-0.0290	0.0002	-0.0008	-0.0430
52	19	C	S	0.4938	-0.0004	0.0002	0.4990
53	19	C	PR	0.0044	0.0007	-0.0020	0.3329
54	19	C	PY	-0.0750	0.0001	0.0004	0.4497
55	19	C	PZ	0.1951	0.0001	-0.0003	-0.6412
56	20	H	S	1.0252	0.0020	0.0000	-0.0321
57	21	H	S	0.4088	1.0069	-0.0300	-0.0005
58	22	H	S	0.0000	-0.0360	0.9961	0.0007
59	23	H	S	-0.0321	-0.0005	0.0007	1.0041

TOTAL ENERGY = -132.8123921730

BINDING ENERGY = -10.8436302360 A.U.

1 H
2 H
3 H
4 C
5 H
6 H
7 C
8 C
9 C
10 C
11 C
12 C
13 C
14 C
15 H
16 H
17 C
18 H
19 C
20 C
21 H
22 H
23 H

DIPOLE MOMENTS

COMPONENTS	X	Y	Z
DESIPTIES	1.01864	-0.14308	2.60331
S-P	-0.28090	-3.89612	0.35374
P-D	0.00000	0.00000	0.00000
TOTAL	0.73566	-18.00000	3.15708

DIPOLE MOMENT = 12.44729 DEBYES

C₃

			1	2	3	4	5	6	7	8	9	10	11
1	1	H	S	-0.0044	-0.0173	-0.0252	-0.0261	0.0072	0.0719	-0.0012	0.0747	-0.1002	-0.0085
2	2	H	S	-0.0044	-0.0782	-0.1029	-0.0306	0.0282	0.0355	-0.0452	0.0010	-0.0094	-0.0089
3	3	H	S	0.0173	0.1020	0.0220	0.0234	-0.0275	-0.0281	-0.0552	0.0330	0.0317	0.0258
4	4	Q	PE	-0.0252	-0.0368	0.0234	0.0073	-0.1463	0.1317	-0.0918	0.1070	-0.3833	-0.1666
5	4	Q	PE	-0.0581	0.1282	-0.0275	-0.1463	1.1310	-0.2530	-0.5182	0.1818	-0.5099	-0.1068
6	4	Q	PE	-0.0572	-0.0355	-0.0281	0.1317	-0.2530	1.7444	0.1853	0.0833	-0.1361	0.1310
7	4	Q	PE	0.0719	-0.0462	-0.1052	-0.3618	-0.0362	0.1853	1.5443	0.1689	-0.3603	-0.0794
8	5	C	S	0.0012	0.0010	-0.0030	0.1070	0.3618	0.0893	0.1689	0.1434	0.0720	0.0188
9	5	C	PE	0.0787	-0.0094	0.0117	-0.3833	-0.5699	-0.1561	-0.3493	0.0720	0.0906	-0.0223
10	5	C	PE	-0.1502	-0.0009	0.0136	-0.0463	0.1310	-0.0784	0.0108	-0.0223	0.0467	-0.0249
11	5	C	PE	-0.0085	-0.0081	0.0258	-0.1046	-0.2628	-0.0555	0.0225	0.0234	-0.0300	-0.0026
12	6	H	S	-0.0306	-0.0042	0.0166	-0.0119	0.0341	-0.1174	-0.0463	0.0542	0.0101	0.0230
13	7	H	S	0.0037	-0.0340	-0.0750	0.0201	-0.0231	-0.0110	0.0188	-0.0037	0.0088	0.0024
14	8	C	S	-0.0124	-0.4904	-0.0049	-0.0173	0.0392	-0.0309	-0.0024	0.0238	-0.0207	-0.0177
15	8	C	PE	-0.0240	-0.2396	-0.0101	-0.0361	0.0532	-0.0246	-0.0246	-0.0398	-0.0464	-0.0234
16	8	C	PE	-0.0062	-0.2763	-0.0050	-0.0200	0.0153	0.0108	-0.0250	0.0050	-0.0072	-0.0018
17	8	C	PE	-0.0010	-0.7834	0.0005	0.0169	0.0132	-0.0177	-0.0012	-0.0029	0.0037	-0.0024
18	9	C	S	0.0473	0.0072	0.4748	0.1848	-0.2184	-0.2333	0.2094	0.0197	-0.0408	-0.0151
19	9	C	PE	0.0437	0.0122	0.2716	0.2282	-0.1240	-0.2485	0.3241	0.0318	-0.0523	-0.0440
20	9	C	PE	0.0437	0.0056	0.1281	0.2230	-0.2459	-0.1217	0.3203	0.0753	-0.0314	-0.0490
21	9	C	PE	-0.0207	-0.0105	0.7029	-0.2436	0.2874	0.2018	-0.2094	-0.0172	-0.0147	0.0047
22	10	H	S	-0.0391	0.0043	0.0087	0.0365	-0.0145	-0.0711	-0.0782	0.0114	0.1822	-0.4788
23	11	H	S	0.0028	0.1106	-0.0046	0.0080	-0.0121	-0.0150	0.0182	0.0015	-0.0002	-0.0006
24	12	C	S	0.0074	-0.0009	0.0032	0.0331	-0.0252	-0.0272	0.0440	0.0012	0.0013	-0.0020
25	12	C	PE	0.0083	0.0139	0.0112	0.0208	-0.0110	-0.0187	0.0371	0.0017	-0.0013	-0.0041
26	12	C	PE	0.0037	0.0015	0.0005	0.0234	-0.0128	-0.0187	0.0300	0.0014	-0.0006	-0.0028
27	12	C	PE	-0.0027	-0.0049	-0.0033	-0.0002	-0.0001	-0.0004	-0.0004	0.0002	0.0000	0.0011
28	13	C	S	0.0028	-0.0022	-0.0144	-0.0043	-0.0270	0.0080	0.0273	0.0024	-0.0112	0.0046
29	13	C	PE	-0.0070	-0.0103	-0.0009	-0.0363	0.0089	0.0048	-0.0330	0.0043	-0.0119	0.0005
30	13	C	PE	-0.0010	-0.0015	-0.0115	-0.0102	-0.0203	0.0045	0.0122	0.0070	-0.0170	0.0051
31	13	C	PE	0.0027	-0.0030	-0.0137	0.0234	-0.0290	0.0252	0.0139	-0.0050	0.0050	0.0026
32	14	H	S	-0.0026	-0.0075	0.1134	-0.0271	0.0241	0.0410	-0.0423	-0.0050	-0.0066	0.0005
33	15	Q	S	0.0094	0.0020	0.0000	0.0019	-0.0015	-0.0025	0.0024	-0.0001	0.0004	-0.0001
34	15	Q	PE	0.0081	0.0088	-0.0055	0.0015	-0.0011	-0.0024	0.0020	0.0002	0.0001	-0.0002
35	15	Q	PE	0.0015	0.0105	-0.0045	0.0057	-0.0045	-0.0060	0.0073	-0.0005	0.0011	-0.0002
36	15	Q	PE	0.0040	-0.0041	0.0134	0.0104	-0.0104	-0.0083	0.0127	-0.0017	0.0031	0.0000
37	16	C	S	-0.0047	-0.0342	0.0031	-0.0137	0.0140	0.0175	-0.0184	0.0023	-0.0048	-0.0007
38	16	C	PE	-0.0081	-0.0147	0.0071	-0.0018	0.0014	0.0018	-0.0028	-0.0001	-0.0001	-0.0008
39	16	C	PE	-0.0047	-0.0444	0.0035	-0.0144	0.0145	0.0154	-0.0204	0.0020	-0.0030	-0.0004
40	16	C	PE	-0.0045	-0.0002	-0.0091	-0.0114	0.0115	0.0129	-0.0120	0.0028	-0.0040	-0.0007
41	17	C	S	-0.0087	0.0069	-0.0280	0.0084	-0.0055	0.0089	0.0054	0.0005	0.0014	-0.0009
42	17	C	PE	-0.0014	-0.0003	0.0029	-0.0040	0.0061	0.0107	-0.0042	0.0005	-0.0018	0.0001
43	17	C	PE	-0.0004	-0.0071	-0.0104	0.0130	-0.0088	-0.0304	0.0068	-0.0002	0.0031	-0.0013
44	17	C	PE	0.0031	0.0060	-0.0060	0.0082	-0.0120	0.0017	0.0110	-0.0110	0.0025	0.0014
45	18	Q	S	0.0005	-0.0002	0.0033	0.0015	-0.0009	-0.0025	0.0013	-0.0005	0.0003	0.0001
46	18	Q	PE	0.0003	0.0004	-0.0060	0.0007	-0.0024	0.0032	0.0013	-0.0001	0.0002	-0.0004
47	18	Q	PE	0.0002	-0.0002	0.0166	-0.0035	0.0030	0.0042	-0.0013	0.0000	0.0018	0.0005
48	18	Q	PE	-0.0036	-0.0121	0.0076	-0.0119	0.0121	0.0025	-0.0123	0.0023	-0.0038	-0.0011
49	19	H	S	-0.0007	0.0004	-0.0030	-0.0052	-0.0002	0.0143	-0.0027	0.0006	-0.0010	0.0008
50	19	H	PE	-0.0011	-0.0007	-0.0032	-0.0053	0.0014	0.0148	-0.0041	0.0010	-0.0020	-0.0013
51	19	H	PE	-0.0004	0.0027	-0.0036	-0.0029	-0.0005	0.0049	-0.0013	0.0005	-0.0011	-0.0007
52	19	H	PE	-0.0003	-0.0102	0.0120	-0.0012	0.0025	-0.0036	-0.0004	0.0001	-0.0001	-0.0006
53	20	H	S	-0.0004	-0.0010	0.0006	-0.0021	0.0010	-0.0052	-0.0017	0.0003	-0.0007	-0.0004
54	21	C	S	0.0000	-0.0021	-0.0011	0.0013	0.0002	-0.0001	0.0000	-0.0001	0.0004	-0.0003
55	21	C	PE	0.0000	-0.0002	-0.0018	0.0005	-0.0002	-0.0003	0.0003	-0.0001	0.0001	-0.0001
56	21	C	PE	0.0000	-0.0034	-0.0011	0.0003	0.0002	-0.0004	0.0003	-0.0002	0.0005	-0.0003
57	21	C	PE	0.0000	-0.0047	-0.0004	0.0001	0.0002	-0.0004	-0.0003	-0.0001	0.0002	-0.0001
58	22	H	S	0.0002	-0.0009	0.0022	0.0007	-0.0002	-0.0023	0.0008	-0.0001	0.0002	-0.0001
59	23	H	S	0.0001	0.0030	-0.0027	0.0008	-0.0009	-0.0001	0.0007	-0.0001	0.0002	0.0000

			12	13	14	15	16	17	18	19	20	21	22
1	1	H	S	-0.0390	-0.0037	-0.0124	-0.0269	-0.0018	-0.0078	-0.0037	-0.0037	-0.0267	-0.0361
2	2	H	S	-0.0042	-0.0346	-0.0004	-0.2306	-0.2263	-0.7634	-0.0072	-0.0122	-0.0096	-0.0160
3	3	H	S	-0.0146	-0.0750	-0.0000	-0.0161	-0.0006	-0.0005	-0.4966	-0.2716	-0.1291	-0.7629
4	4	Q	S	-0.0119	-0.0201	-0.0173	-0.0361	-0.0260	-0.1668	-0.2262	-0.2230	-0.0839	-0.0365
5	4	Q	PK	-0.0341	-0.0221	-0.0362	-0.0532	-0.0153	-0.2184	-0.1260	-0.2450	-0.1878	-0.0145
6	4	U	PT	-0.0174	-0.0118	-0.0326	-0.0246	-0.0160	-0.0177	-0.2333	-0.2885	-0.1217	-0.7010
7	4	Q	PZ	-0.0463	-0.0100	-0.0024	-0.0268	-0.0206	-0.0012	-0.2696	-0.3391	-0.3200	-0.0762
8	5	C	S	-0.0042	-0.0037	-0.0238	-0.0798	-0.0050	-0.0029	-0.0197	-0.0318	-0.0253	-0.0172
9	5	C	PK	-0.0101	-0.0008	-0.0297	-0.0484	-0.0072	-0.0037	-0.0068	-0.0523	-0.0314	-0.0147
10	5	C	PT	-0.0230	-0.0024	-0.0177	-0.0234	-0.0018	-0.0024	-0.0151	-0.0460	-0.0050	-0.0047
11	5	C	PZ	-0.0292	-0.0046	-0.0005	-0.0183	-0.0064	-0.0024	-0.0081	-0.0323	-0.0154	-0.0023
12	6	H	S	-0.0146	-0.0037	-0.0020	-0.0066	-0.0021	-0.0010	-0.0008	-0.0230	-0.0105	-0.0303
13	7	H	S	-0.0037	-0.0050	-0.0489	-0.2092	-0.0007	-0.0496	-0.0007	-0.0232	-0.0363	-0.0046
14	8	C	S	-0.0020	-0.0499	-0.0868	-0.0380	-0.0024	-0.0109	-0.2406	-0.0184	-0.1318	-0.0130
15	8	C	PK	-0.0046	-0.2792	-0.0389	-0.1304	-0.0088	-0.0040	-0.4509	-0.0576	-0.2063	-0.0630
16	8	C	PT	-0.0021	-0.0097	-0.0024	-0.0489	-0.0163	-0.0054	-0.0454	-0.0317	-0.0099	-0.0031
17	8	C	PZ	-0.0010	-0.0496	-0.0100	-0.0040	-0.0043	-0.0066	-0.0409	-0.0007	-0.0293	-0.0153
18	9	C	S	-0.0208	-0.0007	-0.2406	-0.4509	-0.0454	-0.0409	-0.0667	-0.0149	-0.0308	-0.0424
19	9	C	PK	-0.0230	-0.0232	-0.0184	-0.0537	-0.0317	-0.0007	-0.0148	-0.0413	-0.1097	-0.3002
20	9	C	PT	-0.0105	-0.0363	-0.1310	-0.2063	-0.1325	-0.0293	-0.0308	-0.1997	-0.0450	-0.0263
21	9	C	PZ	-0.0303	-0.0068	-0.0379	-0.0030	-0.0008	-0.1563	-0.0424	-0.0302	-0.0063	-0.0331
22	10	H	S	-0.0395	-0.0020	-0.0130	-0.0250	-0.0001	-0.0007	-0.0424	-0.0211	-0.0363	-0.0331
23	11	H	S	-0.0015	-0.0376	-0.0010	-0.0140	-0.0183	-0.0009	-0.0291	-0.0034	-0.0110	-0.0019
24	12	C	S	-0.0017	-0.0043	-0.2706	-0.1346	-0.4823	-0.0008	-0.0273	-0.0585	-0.0482	-0.0064
25	12	C	PK	-0.0005	-0.0566	-0.1119	-0.1227	-0.1170	-0.0242	-0.0219	-0.0348	-0.0120	-0.0034
26	12	C	PT	-0.0014	-0.0234	-0.0090	-0.1613	-0.0141	-0.1444	-0.0267	-0.1124	-0.0035	-0.0191
27	12	C	PZ	-0.0006	-0.0130	-0.0770	-0.0950	-0.1462	-0.1366	-0.0136	-0.0015	-0.0125	-0.0007
28	13	C	S	-0.0042	-0.0748	-0.0235	-0.0257	-0.0396	-0.0008	-0.2458	-0.0193	-0.4564	-0.1223
29	13	C	PK	-0.0025	-0.0455	-0.0166	-0.0168	-0.1132	-0.0168	-0.2038	-0.1093	-0.2379	-0.0731
30	13	C	PT	-0.0049	-0.0563	-0.0207	-0.0081	-0.0307	-0.0276	-0.3777	-0.0231	-0.2516	-0.1866
31	13	C	PZ	-0.0004	-0.0146	-0.0127	-0.0050	-0.0132	-0.0168	-0.1128	-0.0323	-0.2267	-0.0989
32	14	H	S	-0.0060	-0.0295	-0.0271	-0.0101	-0.0157	-0.0059	-0.0024	-0.0212	-0.0074	-0.0188
33	15	Q	S	-0.0002	-0.0026	-0.0074	-0.0009	-0.0077	-0.0018	-0.0034	-0.0018	-0.0006	-0.0008
34	15	Q	PK	-0.0003	-0.0028	-0.0181	-0.0043	-0.0007	-0.0021	-0.0110	-0.0078	-0.0005	-0.0013
35	15	Q	PT	-0.0009	-0.0008	-0.0052	-0.0112	-0.0274	-0.0018	-0.0064	-0.0005	-0.0002	-0.0005
36	15	Q	PZ	-0.0009	-0.0167	-0.0084	-0.0274	-0.0373	-0.0050	-0.0136	-0.0085	-0.0023	-0.0072
37	16	C	S	-0.0024	-0.0289	-0.0002	-0.0334	-0.0320	-0.0052	-0.0481	-0.0220	-0.0253	-0.0063
38	16	C	PK	-0.0005	-0.0218	-0.1015	-0.0043	-0.0007	-0.0021	-0.0110	-0.0078	-0.0005	-0.0013
39	16	C	PT	-0.0021	-0.0799	-0.0079	-0.0310	-0.0343	-0.0075	-0.0493	-0.0194	-0.0103	-0.0034
40	16	C	PZ	-0.0015	-0.0115	-0.0000	-0.0361	-0.0340	-0.0074	-0.0239	-0.0248	-0.0079	-0.0148
41	17	C	S	-0.0047	-0.0322	-0.0044	-0.0203	-0.0352	-0.0021	-0.0017	-0.0059	-0.0393	-0.0086
42	17	C	PK	-0.0011	-0.0037	-0.0006	-0.0147	-0.0029	-0.0012	-0.0007	-0.0104	-0.0028	-0.0019
43	17	C	PT	-0.0053	-0.0354	-0.0456	-0.0213	-0.0238	-0.0024	-0.0120	-0.0245	-0.0484	-0.0120
44	17	C	PZ	-0.0063	-0.0208	-0.0155	-0.0233	-0.0141	-0.0115	-0.0022	-0.0224	-0.0361	-0.0084
45	18	Q	S	-0.0002	-0.0044	-0.0020	-0.0028	-0.0004	-0.0003	-0.0077	-0.0004	-0.0009	-0.0021
46	18	Q	PK	-0.0001	-0.0005	-0.0006	-0.0008	-0.0005	-0.0007	-0.0176	-0.0005	-0.0274	-0.0054
47	18	Q	PT	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001
48	18	Q	PZ	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001
49	19	H	S	-0.0018	-0.0114	-0.0318	-0.0128	-0.0462	-0.0094	-0.0332	-0.0333	-0.0464	-0.0148
50	19	H	PK	-0.0020	-0.0110	-0.0071	-0.0105	-0.0453	-0.0068	-0.0332	-0.0333	-0.0464	-0.0148
51	19	H	PT	-0.0009	-0.0095	-0.0300	-0.0129	-0.0404	-0.0123	-0.0271	-0.0303	-0.0322	-0.0126
52	19	H	PZ	-0.0008	-0.0011	-0.0186	-0.0120	-0.0326	-0.0024	-0.0152	-0.0065	-0.0252	-0.0027
53	20	H	S	-0.0008	-0.0041	-0.0059	-0.0028	-0.0000	-0.0018	-0.0094	-0.0021	-0.0130	-0.0037
54	21	C	S	-0.0008	-0.0036	-0.0047	-0.0047	-0.0012	-0.0028	-0.0057	-0.0021	-0.0122	-0.0039
55	21	C	PK	-0.0001	-0.0009	-0.0012	-0.0013	-0.0012	-0.0008	-0.0048	-0.0122	-0.0034	-0.0040
56	21	C	PT	-0.0011	-0.0052	-0.0100	-0.0075	-0.0020	-0.0008	-0.0048	-0.0122	-0.0034	-0.0040
57	21	C	PZ	-0.0001	-0.0002	-0.0062	-0.0062	-0.0018	-0.0008	-0.0018	-0.0008	-0.0008	-0.0001
58	22	H	S	-0.0002	-0.0034	-0.0006	-0.0049	-0.0144	-0.0022	-0.0004	-0.0020	-0.0008	-0.0017
59	23	H	S	-0.0002	-0.0023	-0.0010	-0.0001	-0.0017	-0.0008	-0.0011	-0.0009	-0.0028	-0.0003

			23	24	25	26	27	28	29	30	31	32	33	
1	1	H	S	0.0220	0.0074	0.0043	0.0030	-0.0027	0.0028	-0.0078	-0.0010	0.0027	-0.0026	0.0006
2	2	H	0	0.1100	-0.0000	0.0130	0.0510	0.0000	-0.0022	-0.0103	0.0015	0.0230	-0.0075	0.0020
3	3	H	0	-0.0040	-0.0032	0.0112	0.0065	-0.0233	-0.0100	-0.0200	-0.0110	-0.0137	0.1134	0.0000
4	4	Q	S	0.0000	0.0331	0.0200	0.0234	-0.0002	-0.0043	-0.0303	-0.0102	0.0234	-0.0271	0.0010
5	4	Q	PX	-0.0121	-0.0252	-0.0110	-0.0128	-0.0001	-0.0270	0.0000	-0.0203	-0.0200	0.0241	-0.0015
6	4	Q	PZ	-0.0136	-0.0272	-0.0107	-0.0107	-0.0004	0.0000	0.0000	0.0000	0.0222	0.0241	-0.0025
7	4	Q	PZ	0.0102	0.0440	0.0371	0.0300	-0.0094	0.0273	-0.0334	0.0122	0.0130	-0.0023	0.0024
8	5	C	S	0.0015	0.0012	0.0017	0.0014	0.0002	0.0024	0.0043	0.0070	-0.0050	-0.0005	-0.0001
9	5	C	PX	-0.0002	-0.0013	-0.0013	-0.0000	0.0000	-0.0012	-0.0110	-0.0170	0.0055	-0.0000	0.0000
10	5	C	PZ	-0.0000	-0.0020	-0.0041	-0.0020	0.0004	-0.0021	-0.0131	-0.0064	0.0027	-0.0035	0.0004
11	5	C	PZ	0.0010	0.0055	0.0073	0.0002	-0.0010	-0.0031	-0.0131	-0.0064	0.0027	-0.0035	0.0004
12	6	H	0	0.0015	0.0017	0.0005	0.0014	0.0000	-0.0042	-0.0055	-0.0040	-0.0000	-0.0000	0.0000
13	7	H	0	-0.0770	0.0043	0.0040	-0.0012	-0.0130	0.0746	-0.0055	0.0063	0.0140	0.0200	0.0020
14	8	C	S	-0.0010	0.2300	-0.1110	0.0000	-0.0770	0.0235	-0.0100	0.0207	0.0127	-0.0271	-0.0074
15	8	C	PX	-0.0140	-0.1340	0.1027	-0.1013	0.0050	0.0207	0.0100	0.0001	-0.0050	-0.0101	0.0000
16	8	C	PZ	-0.0103	-0.0323	0.1170	-0.0141	0.1042	-0.0300	0.1132	-0.0357	-0.0132	0.0107	-0.0077
17	8	C	PZ	0.0040	0.0000	-0.0242	0.1004	0.1304	-0.0000	0.0100	-0.0270	0.0100	0.0050	-0.0015
18	9	C	S	-0.0201	-0.0273	0.0210	-0.0347	-0.0130	0.2030	-0.3777	0.1120	0.0020	-0.0020	-0.0020
19	9	C	PX	0.0034	-0.0003	-0.0340	-0.1124	-0.0015	0.1093	0.0311	0.0123	0.0212	0.0010	0.0010
20	9	C	PZ	0.0110	-0.0042	-0.1200	-0.0035	0.0125	-0.0044	-0.2370	-0.0510	-0.2307	-0.0074	-0.0000
21	9	C	PZ	-0.0010	0.0004	0.0107	0.0101	0.0232	-0.1223	-0.1731	-0.1000	0.0000	-0.0100	0.0000
22	10	H	S	-0.0032	-0.0047	-0.0034	-0.0023	0.0007	0.0040	0.0131	0.0007	0.0003	0.0002	-0.0005
23	11	H	S	0.0027	0.0040	0.0270	-0.0007	0.0300	-0.0051	-0.0071	0.0001	-0.0002	0.1202	0.0134
24	12	C	S	0.0040	0.0010	-0.1202	0.0001	0.0027	0.1024	-0.3030	-0.0100	0.1050	0.0017	0.0002
25	12	C	PX	0.0070	-0.1202	0.1000	-0.0030	0.0030	-0.3030	-0.0071	0.0004	0.2303	0.0000	0.0100
26	12	C	PZ	-0.0007	0.0001	-0.0030	0.0001	0.0001	-0.0030	-0.0030	-0.0030	-0.0030	-0.0030	-0.0030
27	12	C	PZ	0.0030	0.0027	0.0030	0.0004	0.0034	-0.1004	0.2471	0.0001	0.0001	0.0001	0.0001
28	13	C	S	-0.0001	0.1024	0.3000	-0.0030	-0.1004	0.0043	0.1000	-0.0073	0.0010	0.0027	0.0127
29	13	C	PX	-0.0071	-0.3030	-0.0071	0.1000	0.2471	0.1000	0.1150	0.0020	0.0040	-0.0070	-0.0073
30	13	C	PZ	0.0001	-0.0100	0.0004	-0.0001	-0.0001	-0.0073	0.0020	0.0070	-0.0100	-0.0137	-0.0070
31	13	C	PZ	-0.0002	0.1000	0.2303	-0.0030	0.0707	0.0010	0.0070	-0.0100	0.0030	-0.0002	0.0003
32	14	H	S	0.1202	0.0017	0.0000	-0.0005	0.0000	0.0027	-0.0070	-0.0137	0.0001	0.0002	0.0000
33	15	D	S	0.0134	0.0042	0.0100	-0.0103	0.0024	0.0127	-0.0273	-0.0070	0.0003	0.0000	1.7001
34	15	D	PX	0.0040	-0.0005	0.0000	-0.0003	0.0024	0.0142	-0.0000	-0.0000	0.0100	0.0000	-0.3030
35	15	D	PZ	-0.0002	-0.0030	0.0003	0.0003	0.0001	-0.0003	0.0000	-0.0013	0.0070	0.0100	-0.1030
36	15	D	PZ	-0.1310	-0.0000	0.0003	0.0100	0.0000	-0.1174	-0.0121	0.0000	0.0000	0.0000	-0.1574
37	16	H	S	0.0101	0.3110	-0.0027	-0.2770	-0.1001	0.0100	-0.0003	0.0000	-0.0002	-0.0040	0.2503
38	16	H	PX	-0.0103	0.1100	0.0000	-0.1747	-0.1101	0.0101	-0.0003	-0.0130	-0.0130	-0.0002	-0.3702
39	16	H	PZ	-0.0110	0.0110	0.3030	-0.2094	-0.2094	0.0031	-0.0034	0.0020	0.0211	-0.0022	-0.1053
40	16	H	PZ	0.0003	0.1100	0.1000	-0.1000	0.1100	-0.0000	0.0747	0.0000	0.0102	-0.0100	-0.1500
41	17	C	S	-0.0233	0.0140	0.0307	0.0211	0.0020	0.1100	-0.1001	-0.0000	0.1570	0.0121	0.0100
42	17	C	PX	-0.0005	-0.0003	0.0730	0.3030	-0.0100	-0.0230	0.1402	0.0032	-0.0371	0.0150	-0.0241
43	17	C	PZ	-0.0010	0.0000	0.0000	-0.0002	-0.0103	0.1335	0.2530	-0.0003	0.2427	-0.0040	-0.0000
44	17	C	PZ	0.0000	0.0130	0.0007	-0.0300	0.0000	-0.0000	-0.0022	0.0111	0.1000	-0.1012	0.0017
45	18	U	S	0.0004	0.0120	0.0201	-0.0110	-0.0002	0.0000	-0.0211	-0.0001	-0.0025	0.0130	-0.0000
46	18	U	PX	-0.0003	-0.0110	-0.0002	0.0003	0.0173	-0.0132	-0.0002	0.0000	0.0141	-0.0030	0.0003
47	18	U	PZ	0.0020	-0.0001	0.0121	-0.0040	-0.0120	-0.0003	-0.0077	-0.0030	-0.0030	0.0000	-0.0000
48	18	U	PZ	-0.0014	-0.0030	-0.1007	0.0330	0.0000	0.0140	0.0000	-0.0153	-0.0030	0.1300	-0.0032
49	19	H	S	-0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
50	19	H	PX	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
51	19	H	PZ	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000
52	20	H	S	0.0034	0.0024	-0.0105	-0.0000	-0.0020	-0.0061	-0.0111	0.0135	-0.0037	-0.0047	0.0042
54	21	C	S	-0.0001	0.0000	0.0003	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	0.0107	0.0007	-0.1000
55	21	C	PX	-0.0000	0.0000	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
56	21	C	PZ	0.0000	0.0000	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
57	21	C	PZ	0.0000	-0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
58	22	H	S	-0.0100	-0.0005	0.0004	0.0000	0.0000	0.0010	0.0000	-0.0000	-0.0000	0.0100	0.0030
59	23	H	S	0.0120	-0.0017	0.0074	0.0001	0.0007	-0.0132	0.0000	-0.0037	0.0034	-0.0125	0.0024

			34	35	36	37	38	39	40	41	42	43	44	
1	I	H	S	0.0001	0.0015	0.0048	-0.0047	-0.0001	-0.0047	-0.0048	-0.0007	-0.0014	-0.0004	0.0031
2	Z	H	S	0.0008	0.0105	-0.0041	-0.0342	-0.0147	-0.0446	-0.0062	0.0006	0.0063	0.0071	0.0068
3	Z	H	S	-0.0055	-0.0045	0.0130	0.0031	0.0071	0.0038	-0.0091	-0.0200	0.0029	-0.0394	-0.0060
4	A	D	S	0.0015	0.0057	0.0106	-0.0137	-0.0010	-0.0144	-0.0110	0.0094	-0.0068	0.0130	0.0082
5	A	D	PT	-0.0011	-0.0045	-0.0003	0.0168	0.0014	0.0145	0.0115	-0.0055	-0.0061	-0.0068	-0.0126
6	A	D	PZ	-0.0024	-0.0060	-0.0106	0.0175	0.0018	0.0154	0.0126	-0.0189	0.0107	-0.0384	0.0017
7	A	D	PZ	0.0020	0.0073	0.0127	-0.0184	-0.0029	-0.0204	-0.0120	0.0054	-0.0062	0.0068	0.0110
8	S	C	S	0.0002	-0.0005	-0.0017	0.0023	-0.0001	0.0020	0.0020	0.0005	0.0005	-0.0002	-0.0010
9	S	C	PT	0.0001	0.0011	0.0031	-0.0008	-0.0001	-0.0038	-0.0004	0.0014	-0.0018	0.0021	0.0025
10	S	C	PT	-0.0002	-0.0002	0.0020	-0.0007	0.0001	-0.0004	-0.0007	-0.0000	-0.0006	-0.0013	0.0014
11	S	C	PZ	0.0003	0.0010	0.0025	-0.0030	-0.0008	-0.0037	-0.0022	0.0001	-0.0006	0.0004	0.0006
12	H	H	S	0.0003	0.0000	0.0009	-0.0024	-0.0005	-0.0021	-0.0015	0.0047	-0.0011	0.0053	-0.0003
13	Z	H	S	-0.0020	-0.0050	0.0107	0.0200	0.0210	0.0299	-0.0110	-0.0322	-0.0037	-0.0354	0.0200
14	H	C	S	-0.0105	-0.0052	0.0064	0.0002	-0.0015	-0.0070	0.0000	0.0444	-0.0006	0.0150	-0.0155
15	H	C	PT	0.0112	0.0011	-0.0274	0.0134	-0.0045	0.0310	0.0261	0.0503	0.0167	0.0213	-0.0233
16	H	C	PT	0.0274	0.0020	-0.0373	0.0320	0.0097	0.0363	0.0340	-0.0352	0.0028	-0.0245	0.0224
17	H	C	PZ	-0.0010	0.0000	-0.0050	0.0052	0.0021	-0.0070	-0.0070	0.0021	-0.0012	0.0024	-0.0115
18	H	C	S	-0.0044	-0.0130	-0.0138	-0.0481	0.0110	0.0453	0.0230	-0.0107	0.0007	-0.0120	-0.0025
19	H	C	PT	0.0005	0.0017	0.0005	-0.0220	0.0070	-0.0194	-0.0240	-0.0250	-0.0104	-0.0245	0.0224
20	H	C	PT	-0.0002	0.0001	0.0023	-0.0253	-0.0085	-0.0103	-0.0070	0.0293	0.0024	0.0464	-0.0361
21	H	C	PZ	0.0005	0.0030	0.0072	-0.0063	-0.0013	-0.0034	-0.0140	0.0000	0.0014	0.0120	-0.0084
22	I	H	S	-0.0003	-0.0016	-0.0034	0.0052	0.0006	0.0040	0.0043	-0.0019	0.0025	-0.0024	-0.0014
23	I	H	S	0.0745	0.0482	-0.1310	0.0101	-0.0103	-0.0138	0.0003	-0.0233	-0.0005	-0.0414	0.0000
24	I	C	S	-0.0005	-0.0034	-0.0236	0.3110	0.1102	0.0015	0.1452	-0.0006	0.0003	0.0550	0.0130
25	I	C	PT	0.0095	0.0703	0.0403	-0.2527	0.0400	-0.3550	-0.1685	0.0367	0.0730	0.0466	0.0047
26	I	C	PT	0.0093	0.0663	0.0150	-0.1770	0.1747	-0.3504	-0.1079	0.0211	0.0300	-0.0002	-0.1300
27	I	C	PZ	0.0262	0.0001	-0.0425	-0.1981	-0.1101	-0.2047	0.1314	0.0020	-0.0150	-0.0163	0.0045
28	I	C	S	0.0142	-0.0003	0.0349	0.0150	0.0191	0.0531	-0.0000	0.3126	-0.0238	0.4335	-0.0095
29	I	C	PT	-0.0000	0.0008	-0.1174	0.0205	0.0007	0.0344	0.0747	0.1901	0.1402	0.2536	0.0022
30	I	C	PT	-0.0009	-0.0013	0.0121	0.0284	0.0130	0.0020	0.0240	0.0460	0.0432	-0.4953	0.1011
31	I	C	PZ	0.0190	0.0070	0.0040	-0.0002	-0.0130	0.0211	0.0102	0.1570	0.0071	0.2477	-0.0020
32	I	H	S	0.0099	0.0100	0.0066	-0.0245	-0.0002	-0.4422	-0.0144	0.0121	0.0159	-0.0040	-0.1012
33	I	D	S	-0.3826	-0.1030	0.2553	-0.3702	-0.1574	-0.0000	0.1520	0.0100	-0.0281	-0.0060	0.0017
34	I	D	PT	-1.3144	-0.0740	0.1103	-0.5200	-0.1045	-0.4630	0.0340	0.0000	-0.0000	-0.0100	0.0027
35	I	D	PT	-0.1930	1.0719	0.0510	0.1102	-0.1700	0.2102	-0.2155	0.0030	-0.0010	0.0147	-0.0213
36	I	D	PZ	-0.0740	0.0510	1.3090	0.1810	-0.0872	-0.1103	0.0230	0.0335	-0.0002	-0.0150	-0.0050
37	I	C	S	0.0013	0.1102	0.1910	1.0300	-0.0070	0.0077	-0.0112	-0.0001	-0.0123	-0.0059	0.0001
38	I	C	PT	-0.4200	-0.1700	-0.4072	-0.0070	0.0010	0.0131	0.0079	0.0111	0.0304	0.0000	-0.0000
39	I	C	PT	-0.1045	0.2102	0.2103	0.0207	0.0131	0.0268	0.0000	-0.0001	0.0003	-0.0032	-0.0077
40	I	C	PZ	-0.0430	-0.2155	0.0238	-0.0112	0.0470	0.0406	0.0111	-0.0002	-0.0004	0.0004	0.0356
41	I	C	S	0.0436	-0.0030	0.0335	-0.0001	0.0111	-0.0001	-0.0003	1.0304	0.0770	0.0124	0.0155
42	I	C	PT	-0.0002	-0.0010	-0.0105	-0.0123	-0.0304	0.0005	-0.0004	0.0720	0.0705	-0.0059	0.0300
43	I	C	PT	-0.0108	0.0147	-0.0150	-0.0059	0.0000	-0.0032	0.0040	0.0124	0.0000	0.0370	-0.0354
44	I	C	PZ	0.0247	0.0213	-0.0050	0.0001	-0.0000	-0.0077	0.0356	0.0155	0.0305	-0.0354	0.0011
45	I	D	S	-0.0070	0.0035	0.0035	0.0171	0.0220	-0.0107	-0.0025	0.2553	0.3359	-0.2020	0.1300
46	I	D	PT	0.0350	-0.0027	-0.0105	-0.0305	-0.0412	0.0270	-0.4700	0.0000	0.1200	0.1957	0.0000
47	I	D	PT	-0.0051	-0.0070	0.0229	0.0004	0.0153	0.0001	-0.0104	0.2400	0.0200	0.0450	0.2500
48	I	D	PZ	0.0223	-0.0070	0.0050	-0.0340	-0.0130	0.0270	-0.0042	0.1720	-0.0403	0.2500	0.0702
49	I	H	S	-0.0000	0.1070	0.0130	0.2741	0.3200	-0.3300	0.0001	0.2740	-0.3402	-0.2325	-0.0704
50	I	H	PT	0.0524	-0.0026	0.0500	-0.3447	-0.2402	0.4239	-0.0943	0.3557	-0.4405	-0.3500	-0.1477
51	I	H	PT	-0.0350	0.0573	0.0143	0.2719	0.3347	-0.2177	0.0227	0.1700	0.2000	-0.0405	-0.0441
52	I	H	PZ	0.1001	0.0431	0.2157	-0.0595	-0.1424	0.0002	0.3474	0.0000	-0.1030	-0.0232	0.3300
53	Z	H	S	0.0050	-0.0205	0.0004	-0.0320	-0.0417	0.0315	-0.0057	0.0501	-0.0041	-0.0040	-0.0141
54	Z	I	C	S	-0.0127	0.0011	-0.0107	-0.0005	-0.0037	0.0031	0.0000	0.0000	-0.0042	-0.0030
55	Z	I	C	PT	0.0004	-0.0216	0.0047	-0.0015	-0.0027	0.0001	0.0020	0.0034	-0.0016	-0.0042
56	Z	I	C	PT	-0.0000	-0.0210	0.0040	-0.0037	-0.0006	0.0004	0.0015	0.0024	-0.0024	-0.0005
57	Z	I	C	PZ	0.0007	0.0024	-0.0000	-0.0004	0.0002	0.0041	-0.0012	0.0004	0.0014	-0.0004
58	Z	H	S	0.0124	0.0102	-0.0325	0.0201	0.0130	-0.0630	0.0450	-0.0000	0.0006	0.0131	0.0420
59	Z	H	S	-0.0100	-0.0043	0.0370	0.0367	0.0470	-0.0200	-0.0300	-0.0172	0.0328	0.0030	-0.0324

			45	46	47	48	49	50	51	52	53	54	55
1	1	H	S	0.0005	0.0003	0.0002	-0.0036	-0.0067	-0.0011	-0.0004	0.0003	-0.0000	0.0000
2	2	H	S	-0.0002	0.0004	-0.0052	-0.0121	0.0004	-0.0007	0.0027	-0.0102	-0.0021	0.0002
3	3	H	S	0.0033	-0.0006	0.0106	0.0078	-0.0038	-0.0032	-0.0006	0.0128	0.0006	-0.0011
4	4	O	S	0.0015	-0.0007	-0.0035	-0.0118	-0.0082	-0.0053	-0.0026	-0.0102	-0.0021	0.0013
5	4	O	PE	-0.0006	-0.0024	0.0030	0.0121	-0.0002	0.0018	-0.0005	0.0025	0.0010	-0.0002
6	4	O	PE	-0.0025	0.0032	0.0042	0.0025	0.0123	0.0148	0.0060	-0.0138	0.0052	-0.0033
7	4	O	PE	0.0013	0.0013	-0.0013	-0.0123	-0.0017	-0.0041	-0.0013	-0.0004	-0.0017	0.0000
8	8	C	S	-0.0005	-0.0001	0.0000	0.0023	0.0006	0.0010	0.0005	0.0001	0.0003	-0.0001
9	5	C	PE	0.0003	0.0002	-0.0016	-0.0038	-0.0018	-0.0020	-0.0011	-0.0003	-0.0007	0.0004
10	5	C	PE	0.0001	0.0006	0.0008	-0.0011	0.0009	0.0008	0.0007	-0.0006	0.0002	-0.0001
11	5	C	PE	0.0001	-0.0002	-0.0007	0.0023	-0.0013	-0.0013	-0.0009	0.0003	-0.0004	0.0001
12	4	H	S	0.0002	-0.0001	-0.0012	-0.0009	-0.0018	-0.0020	-0.0009	0.0000	-0.0006	0.0001
13	7	H	S	0.0044	-0.0005	0.0107	-0.0087	-0.0114	0.0110	-0.0006	-0.0011	0.0041	0.0030
14	8	C	S	-0.0020	0.0005	-0.0143	0.0108	0.0319	-0.0271	0.0300	0.0194	-0.0050	-0.0047
15	8	C	PE	-0.0026	-0.0008	-0.0040	0.0123	-0.0129	0.0156	-0.0129	-0.0123	0.0024	0.0013
16	8	C	PE	0.0004	0.0005	0.0036	-0.0031	-0.0442	0.0453	-0.0404	-0.0329	0.0090	0.0112
17	8	C	PE	-0.0003	-0.0007	-0.0037	0.0058	0.0094	0.0064	0.0123	0.0024	-0.0010	-0.0002
18	6	C	S	-0.0077	0.0170	-0.0070	-0.0062	0.0352	0.0352	0.0271	-0.0152	0.0094	-0.0097
19	9	C	PE	0.0004	0.0055	0.0008	-0.0181	0.0037	0.0053	0.0033	-0.0063	0.0021	-0.0003
20	6	C	PE	0.0009	-0.0274	0.0009	0.0437	-0.0484	-0.0535	-0.0322	0.0282	-0.0138	0.0122
21	9	C	PE	0.0021	-0.0004	-0.0077	-0.0034	-0.0140	-0.0138	-0.0128	0.0027	-0.0037	0.0035
22	10	H	S	-0.0004	0.0008	0.0009	0.0027	0.0022	0.0036	0.0013	-0.0005	0.0008	0.0006
23	11	H	S	0.0004	-0.0053	0.0230	-0.0014	-0.0200	0.0213	-0.0113	-0.0758	0.0034	0.0001
24	12	C	S	0.0129	-0.0153	-0.0010	-0.0365	-0.0412	-0.0194	-0.0302	-0.0278	0.0020	0.0040
25	12	C	PE	0.0251	-0.0062	0.0121	-0.1097	-0.0562	-0.0332	-0.0114	-0.0033	-0.0105	0.0003
26	12	C	PE	0.0118	0.0083	-0.0009	0.0336	0.0288	-0.0068	-0.0098	0.0071	-0.0088	-0.0091
27	12	C	PE	-0.0002	-0.0173	-0.0125	0.0008	0.0104	0.0105	0.0224	-0.0202	-0.0020	-0.0100
28	13	C	S	0.0040	-0.0132	-0.0063	0.0140	-0.0395	0.0107	-0.0432	0.0213	-0.0001	0.0277
29	13	C	PE	-0.0211	-0.0062	-0.0626	0.0084	0.0011	-0.0278	0.0161	-0.0051	-0.0111	-0.0062
30	13	C	PE	-0.0061	0.0005	0.0077	-0.0153	0.0182	0.0036	-0.0106	-0.0063	0.0135	-0.0080
31	13	C	PE	-0.0048	0.0141	-0.0536	-0.0535	-0.0148	0.0138	-0.0247	-0.0257	-0.0037	0.0157
32	14	H	S	0.0136	-0.0039	0.0456	0.1368	-0.0237	-0.0260	-0.0147	0.0748	-0.0047	0.0007
33	15	O	S	-0.0004	0.0003	0.0018	-0.0032	-0.0010	0.0126	0.0152	0.0144	0.0042	-0.0129
34	15	O	PE	-0.0078	0.0350	-0.0081	-0.0023	-0.0046	0.0034	-0.0356	0.1001	0.0050	-0.0127
35	15	O	PE	0.0035	-0.0027	-0.0079	-0.0270	-0.0028	0.0073	0.0431	-0.0265	0.0011	-0.0216
36	15	O	PE	0.0035	-0.0016	0.0228	0.0066	-0.0138	0.0004	0.0143	-0.2157	0.0004	-0.0107
37	16	C	S	0.0171	-0.0365	0.0004	-0.0346	0.2741	-0.2447	0.2716	-0.0094	-0.0320	0.0065
38	16	C	PE	0.0229	-0.0012	0.0153	-0.0138	0.1200	-0.2002	0.1367	-0.1424	0.0417	-0.0030
39	16	C	PE	0.0107	0.0278	0.0001	0.0205	-0.1388	0.4238	-0.2177	0.0052	0.0315	0.0037
40	16	C	PE	0.0025	0.0227	-0.0104	-0.0043	0.0401	-0.0043	0.0227	0.1674	-0.0057	0.0030
41	17	C	S	0.2553	-0.4306	0.2400	-0.1728	0.2740	0.3957	0.1745	0.0608	0.0541	0.0068
42	17	C	PE	0.3350	-0.3091	0.3391	-0.4043	-0.3092	-0.4405	-0.2620	-0.1830	-0.0841	0.0040
43	17	C	PE	-0.2029	0.1329	0.1450	0.2156	-0.2528	-0.3568	-0.0465	-0.0232	-0.0468	-0.0042
44	17	C	PE	0.1360	-0.1997	0.2599	0.0782	-0.0784	-0.1477	-0.0441	0.3369	-0.0141	-0.0038
45	18	O	S	1.7600	0.3462	-0.2052	0.1401	-0.0020	-0.0092	0.0100	-0.0122	0.0053	-0.0102
46	18	O	PE	0.3462	1.4332	0.3051	-0.0494	0.0888	0.0794	0.0283	0.1812	0.0067	0.0104
47	18	O	PE	-0.0512	0.1011	1.7506	0.0131	0.0084	0.0011	0.0363	-0.0395	0.0006	-0.0096
48	18	O	PE	0.1401	-0.0494	0.0131	1.3062	0.0274	0.0000	-0.0006	-0.2105	-0.0017	0.0137
49	19	H	S	-0.0020	0.0038	0.0004	0.0274	1.1837	0.0040	0.0030	-0.0070	-0.0008	0.2548
50	19	H	PE	-0.0002	0.0706	0.0011	0.0508	0.0040	1.1895	-0.0030	-0.0068	0.0457	-0.0114
51	19	H	PE	0.1950	0.0203	0.0343	0.0008	0.0030	0.0040	1.1194	-0.0070	-0.0003	-0.0104
52	19	H	PE	-0.0122	0.0112	-0.0365	-0.2105	-0.0079	-0.0048	-0.0170	1.7038	0.0038	-0.0118
53	20	H	S	0.0053	0.0007	0.0006	-0.0017	-0.0004	0.0457	-0.0043	-0.0038	0.0040	-0.0020
54	20	H	PE	-0.0102	0.0104	-0.0090	0.0137	0.2548	-0.0514	-0.0184	-0.0148	0.0078	-0.0118
55	21	C	PE	-0.0010	0.0050	-0.0011	0.0006	0.0040	0.1384	-0.1045	-0.0112	-0.0230	-0.0114
56	21	C	PE	-0.3772	-0.0005	-0.0253	0.0109	0.0532	-0.1005	-0.0661	-0.0344	-0.1761	-0.0020
57	21	C	PE	-0.0026	0.0101	-0.0036	-0.0158	-0.0206	-0.0113	-0.0338	0.1529	-0.0009	-0.0023
58	22	H	S	-0.0010	0.0129	-0.0128	-0.0388	-0.0086	-0.0366	0.0004	0.1030	-0.0314	0.4994
59	23	H	S	0.0010	-0.0108	0.0018	0.0406	-0.0041	-0.0072	0.0006	-0.0099	-0.0202	0.4008

1	1	H	S	0.0080	0.0000	0.0002	0.0001
2	2	H	S	-0.0034	-0.0007	-0.0008	0.0030
3	3	H	S	-0.0013	0.0004	0.0022	-0.0027
4	4	O	S	0.0023	0.0001	0.0007	0.0004
5	4	O	PX	0.0002	0.0002	-0.0002	-0.0009
6	4	O	PY	-0.0008	-0.0005	-0.0023	-0.0001
7	4	O	PZ	0.0003	-0.0003	0.0008	0.0007
8	8	C	S	-0.0002	-0.0001	-0.0001	-0.0001
9	8	C	PX	0.0009	0.0002	0.0002	0.0002
10	8	C	PY	-0.0002	0.0000	0.0001	0.0001
11	8	C	PZ	0.0003	0.0001	0.0002	0.0000
12	6	H	S	0.0011	0.0001	0.0002	0.0002
13	7	H	S	0.0002	0.0002	-0.0034	-0.0023
14	8	C	S	-0.0109	0.0002	0.0004	0.0010
15	8	C	PX	0.0075	0.0002	-0.0009	-0.0001
16	8	C	PY	0.0200	-0.0010	-0.0144	-0.0017
17	8	C	PZ	-0.0046	0.0009	0.0032	0.0006
18	9	C	S	-0.0124	-0.0010	-0.0054	0.0011
19	9	C	PX	-0.0024	0.0000	-0.0020	0.0000
20	9	C	PY	0.0226	0.0024	0.0088	-0.0028
21	9	C	PZ	0.0069	0.0018	0.0017	-0.0053
22	10	H	S	-0.0009	-0.0001	-0.0004	-0.0001
23	11	H	S	0.0006	0.0001	-0.0164	0.0129
24	12	C	S	0.0047	-0.0011	-0.0008	-0.0017
25	12	C	PX	0.0018	0.0039	0.0045	0.0074
26	12	C	PY	-0.0302	0.0039	0.0095	0.0041
27	12	C	PZ	-0.0305	-0.0008	0.0008	0.0067
28	13	C	S	0.0475	0.0050	0.0018	-0.0032
29	13	C	PX	-0.0114	0.0025	0.0070	0.0070
30	13	C	PY	0.0422	-0.0070	-0.0058	-0.0037
31	13	C	PZ	0.0249	-0.0059	-0.0044	0.0034
32	10	H	S	0.0031	0.0000	0.0166	-0.0125
33	10	C	S	-0.0068	0.0009	0.0039	0.0024
34	10	C	PX	-0.0056	0.0007	0.0126	-0.0106
35	10	C	PY	-0.0218	0.0024	0.0162	-0.0093
36	10	C	PZ	-0.0240	-0.0060	-0.0325	0.0070
37	10	C	S	0.0007	-0.0004	0.0001	0.0067
38	10	C	PX	-0.0232	0.0002	0.0138	0.0470
39	10	C	PY	-0.0066	0.0001	-0.0428	-0.0292
40	10	C	PZ	0.0066	-0.0012	0.0456	-0.0360
41	17	C	S	0.0010	0.0004	-0.0008	-0.0172
42	17	C	PX	0.0024	0.0014	0.0005	0.0325
43	17	C	PY	-0.0024	-0.0000	0.0131	0.0036
44	17	C	PZ	-0.0048	-0.0054	0.0425	-0.0324
45	10	C	S	-0.0072	-0.0020	-0.0010	0.0010
46	10	C	PX	-0.0008	0.0101	0.0129	-0.0186
47	10	C	PY	-0.0283	-0.0034	-0.0120	0.0019
48	10	C	PZ	0.0169	-0.0159	-0.0308	0.0004
49	19	H	S	0.0022	0.0005	-0.0009	-0.0041
50	19	H	PX	-0.0008	-0.0113	-0.0368	-0.0072
51	19	H	PY	-0.4441	-0.0339	0.0040	0.0006
52	19	H	PZ	-0.0264	0.1020	0.1030	0.0000
53	20	H	S	-0.1761	-0.0907	-0.0314	-0.0200
54	21	C	S	-0.0020	-0.0033	0.4994	0.4980
55	21	C	PX	-0.0004	0.0008	0.4302	0.2860
56	21	C	PY	0.0023	-0.0039	-0.3202	-0.3569
57	21	C	PZ	-0.0039	0.1623	-0.0610	0.7170
58	22	H	S	-0.3202	-0.0610	1.0093	-0.0007
59	23	H	S	-0.3569	0.7170	-0.0607	1.0000

TOTAL ENERGY = -132.4875015236

BINDING ENERGY = -10.7507475663 A.U.

1 H
2 H
3 H
4 O
5 H
6 H
7 C
8 C
9 C
10 H
11 C
12 C
13 C
14 O
15 O
16 C
17 C
18 N
19 N
20 N
21 C
22 H
23 H

DIPOLE MOMENTS

COMPONENTS	X	Y	Z
DENSITIES	0.24957	1.01463	0.62046
S.P	0.33864	0.13706	1.07016
P.D	0.00006	0.00000	0.00000
TOTAL	0.24964	1.01462	1.07016

DIPOLE MOMENT = 2.66192 DEBYE

BIBLIOGRAPHY

1. H. Standinger, W. Heuer, Ber., 67, 1164 (1934)
2. G.B. Butler, Acc. Chem. Res., 15, 370 (1982)
3. G.B. Butler, R.J. Angelo, J. Am. Chem. Soc., 79, 3128 (1957)
4. P.J. Flory, J. Am. Chem. Soc., 59, 241 (1937)
5. D.S. Breslow, Pure Appl. Chem., 45, 103 (1976)
6. T.F. Gray, Jr., G.B. Butler, J. Macromol. Sci.-Chem., A9(1), 45 (1975)
7. A.L.J. Beckwith, Tetrahedron, 37(18), 3073 (1981)
8. (a) B. Capon, C.W. Rees, Annual Reports, 61, 261 (1964); (b) B. Capon, Quart. Rev., 18, 45 (1964)
9. (a) P. Bischof, Tetrahedron Letters, 1291 (1971); (b) P. Bischof, Helv. Chim. Acta., 63, 1434 (1980)
10. (a) R.D. Rieke, N.A. Moore, J. Org. Chem., 37, 413 (1972); (b) R.D. Rieke, N.A. Moore, Tetrahedron Letters, 2035 (1969)
11. (a) M. Julia, M. Murny, Bull. Soc. Chim. Fr., 1603 (1968); (b) M. Julia, C. Descoins, M. Baillarge, B. Jacquet, D. Ugnen, F.A. Groeger, Tetrahedron, 31, 1737 (1975); (c) A.L.J. Beckwith, T. Lawrence, J. Chem. Soc. Perkin Trans. II, 1535 (1979)
12. (a) A.L.J. Beckwith, W.B. Gara, J. Chem. Soc. Perkin Trans. II, 593, 795 (1975); (b) A.L.J. Beckwith, G.F. Meijs, Ibid. Chem. Commun., 136 (1981)
13. (a) D.L. Struble, A.L.J. Beckwith, G.E. Gream, Tetrahedron Letters 3701 (1968); (b) A.L.J. Beckwith, G.E. Gream, D.L. Struble, Aust. J. Chem., 25, 1081 (1972)
14. A.L.J. Beckwith, "Essays on Free Radical Chemistry" (Chem. Soc. Publ. No. 24, p. 239, Chem. Soc., London, 1970)

15. A.L.J. Beckwith, I.A. Blair, G. Phillipou, *Tetrahedron Letters*, 2251 (1974)
16. T.W. Smith, G.B. Butler, *J. Org. Chem.*, 43, 6 (1978)
17. (a) M. Julia, *Pure Appl. Chem.*, 40, 553 (1974); (b) M. Julia, *Acc. Chem. Res.*, 4, 386 (1971)
18. (a) R.S. Mulliken, *J. Am. Chem. Soc.*, 74, 811 (1952); (b) R.S. Mulliken, *J. Phys. Chem.*, 56, 801 (1952)
19. R.S. Mulliken, *J. Chem. Phys.*, 61, 20 (1964)
20. M.J.S. Dewar, C.C. Thompson, *Tetrahedron Supp.*, No. 7, 97 (1966)
21. (a) E.M. Kosower, *Prog. Phys. Org. Chem.*, 3, 81 (1965)
(b) E.M. Kosower "Introduction to Physical Organic Chemistry" (Wiley, New York, 1968)
22. H.K. Hall, Jr., *Angew. Chem. Int. Ed.*, 22, 440 (1983)
23. R. Foster, "Molecular Complexes," Vol. 2, p. 172 (Crane Russak & Co. Inc., 1974)
24. H.K. Hall, Jr., T. Gotoh, *Polym. Preprints*, 26(1), 34 (1985)
25. G.B. Butler, K.G. Olson, *Macromolecules*, 16, 707 (1983)
26. R.B. Seymour, G.A. Stahl, D.P. Garner, R.D. Knapp, *Polym. Preprints*, 17(1), 216 (1976)
27. Y. Lai, G.B. Butler, *J. Macromol. Sci.-Chem.*, A21 (11 & 12), 1547 (1984)
28. Merck & Co., Inc., "Deuterated NMR Solvents--Handy Reference Data" (Merck & Co., Inc., Quebec, 1978)
29. A.J. Gordo, R.A. Ford, "The Chemists Companion: A Handbook of Practical Data, Techniques and References" (John Wiley & Sons, New York, 1972)
30. L.F. Hatch, T.L. Patton, *J. Am. Chem. Soc.*, 76, 2705 (1954)
31. K. Baucom, Ph.D. Dissertation, University of Florida, 1971
32. K. Ramarajan, K. Ramalingam, D.J. O'Donnell, K.D. Berlin, *Org. Synthesis*, 61, 56 (1983)
33. A.F. Ferris, I.G. Marks, *J. Org. Chem.*, 19, 1971 (1954)
34. P.A. Levene, *Org. Synthesis, Coll*, 10, 12 (1930)

35. R.M. Jacobson, R.A. Raths, J.M. McDonald, J. Org. Chem., 42(15), 2545 (1977)
36. C. Greenwood, H.M.R. Hoffman, J. Org. Chem., 37(4), 611 (1972)
37. R.W. Rosenthal, L.H. Schwartzman, N.P. Greco, R. Proper, J. Org. Chem., 28, 2835 (1963)
38. B.E. Leggetter, R.K. Brown, Canadian J. Chem., 42, 990-1004 (1964)
39. W. Reeve, A. Saddle, J. Am. Chem. Soc., 72, 1251 (1950)
40. R.C. Fuson, B.H. Wojcik, Org. Synthesis, 13, 42 (1944)
41. W. Fickett, H.K. Garner, H.J. Lucas, J. Am. Chem. Soc., 73, 5066 (1951)
42. R.B. Moffett, Org. Synthesis Cum., Vol. 4, 834 (19//)
43. L.S. Boguslavskaya, A.B. Bulovyatava, A.P. Sinekov, V.S. Ettis, Zh. Organiche. Khimii, 7(4), 637 (1971)
44. A.J. Hill, E.J. Fischer, J. Am. Chem. Soc., 44, 2594 (1922)
45. R.M. Silverstein, G.C. Bassler, T.C. Morrill, "Spectrometric Identification of Organic Compounds" (4th Edition, John Wiley & Sons, New York, 1981)
46. (a) J. March, "Advanced Organic Chemistry" pp 342 (3rd Edition, Wiley Interscience, 1985); (b) S. Warren, "Designing Organic Synthesis" (J. Wiley & Sons Ltd., Great Britain, 1979)
47. K. Baucom, Ph.D. research, University of Florida
48. Insensitive nuclei enhanced by polarization transfer
49. M. Turushima, Y. Ando, K. Yetani, Yakugaku Zasshi, 93, 1274 (1973)
50. M. Turushima, Y. Ando, K. Yetani, *ibid*, 93, 1285 (1973)
51. M. Turushima, Y. Ando, K. Yetani, *ibid*, 93, 1294 (1973)
52. Dr. S. Mallakpour, University of Florida
53. (a) No. 22623 "The Sadtler Standard Spectra" (Sadtler Research Laboratories, Inc., U.S.A., 1976); (b) No. 3944 *ibid* (Sadtler Research Laboratories, Inc., U.S.A., 1967)
54. W.C. Herndon, J. Fever, J. Am. Chem. Soc., 90, 5914 (1968)
55. R. Arnaud, D. Faramond-Baud, M. Gelus, Theoret. Chim. Acta., 31, 335 (1973)

56. D.B. Chesnut, P.E.S. Wormer, Theoret. Chim. Acta., 20, 250 (1971)
57. R. Lochmann, T. Weller, Int. J. Quantum Chem., Vol. X, 909 (1976)
58. R. Lochmann, H.J. Hofmann, Int. J. Quantum Chem., Vol. XI, 427 (1977)
59. J.A. Pople, D.L. Beveridge, "Approximate Molecular Orbital Theory" (McGraw Hill, New York, 1970)
60. (a) S. Diner, J.P. Malrien, P. Claverie, Theoret. Chim. Acta., 13, 1 (1969); (b) J.P. Malrien, P. Claverie, S. Diner, Theoret. Chim. Acta., 13, 18 (1969); (c) S. Diner, J.P. Malrien, F. Jordan, M. Gilbert, Theoret. Chim. Acta., 15, 100 (1969); (d) F. Jordan, M. Gilbert, J.P. Malrien, U. Pincetti, Theoret. Chim. Acta., 15, 211 (1969)
61. Publication by Quantum Chemistry Program Exchange, Indiana University, Program No. 220/221
62. J.D. Dandey, P. Claverie, J.P. Malrien, Int. J. Quantum Chem., 8, 1 (1974)
63. (a) J.A. Pople, Santry, Segal, J. Chem. Phys., 43, 5129 (1965); (b) J.A. Pople, G.A. Segal, J. Chem. Phys., 43, 5136 (1965); (c) J.A. Pople, G.A. Segal, J. Chem. Phys., 44, 3289 (1966); (d) D.P. SENTRY, G.A. Segal, J. Chem. Phys., 47, 158 (1967); (e) J.E. Ridley, M. Zerner, Theoret. Chim. Acta., 32, 111 (1973); (f) J.E. Ridley, M. Zerner, Theoret. Chim. Acta., 42, 223 (1976); (g) A.D. Bacon, M. Zerner, Theoret. Chim. Acta., 53, 21 (1979); (h) M. Zerner, G.H. Zeow, R.F. Kirchner, U.T. Mueller-Westerhoff, J. Am. Chem. Soc., 102, 589 (1980)
64. QUIPU uses Quantum Chemistry Program Exchange Programs and the University of Florida, Quantum Theory Project programs and was written by Dr. G. Purvis. It is a local adaptation of the DuPont Molecular Modeling system, TRIBBLE developed by D. Pensak at DuPont's Central Research Division, Wilmington, Del.
65. The Cullen, Zerner version of PCILO by J.P. Daudey
66. G.B. Butler, A. Matsumoto, J. Polym. Sci., Polym. Letters Edition, 9, 167 (1981)
67. G.B. Butler, A. Matsumoto, T. Kitamura, M. Oiwa, J. Polym. Sci., Polym. Chem. Edition, 19, 2531 (1981)

BIOGRAPHICAL SKETCH

Roy Joseph Noel Vaz was born on August 2, 1958, in Bombay, India. In 1974 he obtained the secondary school certificate via Sacred Heart High School, Santa Cruz, and after a year at St. Xavier's College, Bombay, joined the Indian Institute of Technology, Bombay. He obtained the M.S. (5 year integrated) in 1980 and subsequently enrolled at the University of Florida. He was awarded the DuPont teaching award in 1982 and is currently a member of the American MENSA.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



George B. Butler, Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



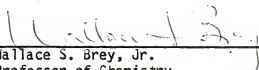
Merle A. Battiste
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Ken B. Wagener
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Wallace S. Brey, Jr.
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Christopher D. Batich
Professor of Materials Science and
Engineering

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August, 1985

Dean, Graduate School